THE PROCEEDINGS OF
THE PHYSICAL SOCIETY

VOL. 49, PART 4 JULY 1, 1937 No. 273

THE SATURATION-DISCRIMINATION OF TWO TRICHROMATS

BY W. D. WRIGHT, D.Sc., A.R.C.S., D.I.C.

AND

F. H. G. PITT, Ph.D., A.R.C.S., D.I.C.,

Imperial College of Science and Technology

Received 21 *October* 1936. *Read* 28 *May* 1937

ABSTRACT. Measurements have been made by the authors to determine the values for their own eyes of log $\{(L_W + L_S)/L_S\}$ for the just-noticeable first step from white for a range of spectral colours.

THIS short paper is supplementary to one⁽¹⁾ published in 1935, in which the detailed characteristics of the authors' colour-vision were tabulated. We expressed some dissatisfaction with the data on saturation-discrimination, not because we doubted the accuracy of the measurements but because, when the first step from the spectral locus was measured, each observation was necessarily made in a different part of the colour field, so that the sensitivity of the eye to colour-differences was itself variable. The results thus represented two variables, namely the sensitivity of the eye and the colour valency of the spectral colours, whereas the latter alone should have been measured. It can be effectively isolated if the first step from white is measured rather than the first step from the spectral locus, since the observations will all be made in practically the same part of the colour triangle.

No very simple way of making the measurements with the Wright colorimeter was available at the time, and the less satisfactory step from the spectral locus was measured instead. A straightforward adaptation of the colorimeter has since been devised and the modification and method of observation have been described by Nelson⁽²⁾. The new data obtained in this way for the authors' eyes are shown in figures 1 and 2. The saturation-discrimination has been represented in the conventional manner as log $\{(L_W + L_S)/L_S\}$, where L_S is the luminosity of the spectral colour that has been mixed with white of luminosity L_W to produce the just-noticeable step. A radiation with a small colour valency will thus give a small value of

$\log \{(L_W + L_S)/L_S\}$, and *vice versa.* The steps were measured relative to the white given by the C.I.E. 1931 S_B source, which has a colour temperature of 4800° K.

The general agreement between the authors' curves and the mean curve given by Martin, Warburton and Morgan[3] is very good. Undoubtedly the most striking feature is the pronounced minimum shown in all the curves; the very close agreement between one observer and another in the wave-length, about 0·57 μ., at which the minimum occurs, is specially noteworthy.

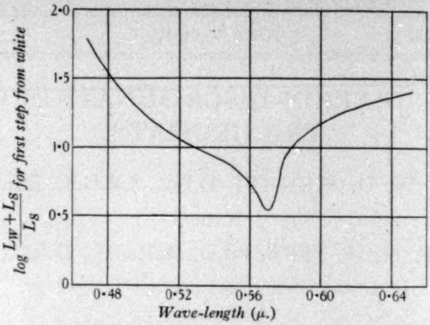


Figure 1. Saturation-discrimination curve for F. H. G. P.

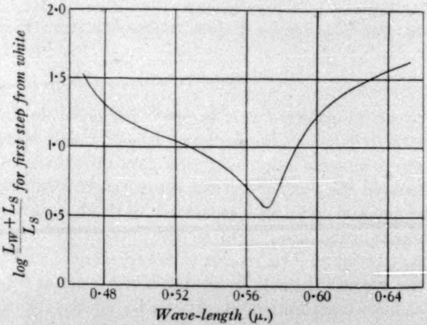


Figure 2. Saturation-discrimination curve for W. D. W.

INDEX SLIP

OF THE

PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 49, 1937, PART 3

SUBJECT INDEX

533.16:546.217

Bond, W N

1936.05.14. The viscosity of air.

Proc. phys. Soc. Lond. **49**, 205–213 (1937).

536.413.2:669.144.24

Owen, E A
Yates, E L

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 3: The thermal expansion of alloys rich in iron.

Proc. phys. Soc. Lond. **49**, 307–314 (1937).

536.413.2:669.144.24

Owen, E A
Yates, E L
Sully, A H

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 5: The variation of thermal expansion with composition.

Proc. phys. Soc. Lond. **49**, 323–325 (1937).

536.491

Buckley, H

1936.08.12. Note on the radiation between two coaxial radiating cylinders.

Proc. phys. Soc. Lond. **49**, 225–229 (1937).

538.22:669.791.5

Bates, L F
Tai, L C

1936.10.27. The magnetic properties of manganese amalgams.

Proc. phys. Soc. Lond. **49**, 230–236 (1937).

539.23

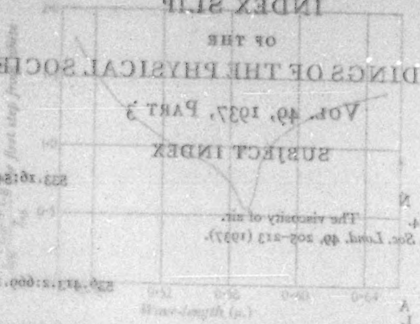
Quarrell, A G

1937.01.22. Structural changes during the growth of metal films.

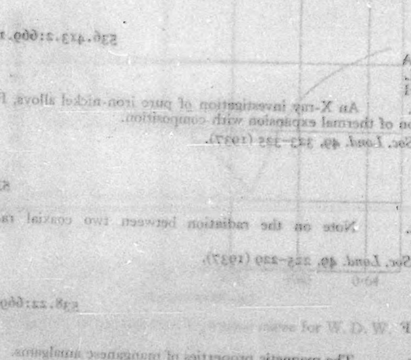
Proc. phys. Soc. Lond. **49**, 279–293 (1937).

[illegible] and six were. The steps were measured relative to the white [illegible] by the C.I.E. [illegible] source, which has a colour temperature of 4800° K.

The general agreement between the authors' curves and the mean curve given



C. P.



[illegible] curve for W. D. W.

by Mazur, [illegible] Undoubtedly the most striking feature [illegible] all the curves; the very close agreement [illegible] the wave-length, about 0·57 μ, at which the [illegible]

541.123.23:669.018

Jones, H

1936.12.16. The phase boundaries in binary alloys, Part 1: The equilibrium between liquid and solid phases.

Proc. phys. Soc. Lond. **49**, 243–249 (1937).

541.123.23:669.35

Jones, H

1936.12.16. The phase boundaries in binary alloys, Part 2: The theory of the α, β phase boundaries.

Proc. phys. Soc. Lond. **49**, 250–257 (1937).

541.183.55:674.045

Barkas, Wilfred W

1936.12.15. Wood-water relationships, Part III. Molecular sorption of water by Sitka spruce wood.

Proc. phys. Soc. Lond. **49**, 237–242 (1937).

546.217:533.16

Bond, W N

1936.05.14. The viscosity of air.

Proc. phys. Soc. Lond. **49**, 205–213 (1937).

546.33:548.73

Dawton, Ralph H V M

1936.12.23. Intensities of X-ray reflections from single crystals of sodium between 120 and 370° K.

Proc. phys. Soc. Lond. **49**, 294–306 (1937).

548.712:669.144.24

Owen, E A
Yates, E L
Sully, A H

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 4: The variation of lattice-parameter with composition.

Proc. phys. Soc. Lond. **49**, 315–322 (1937).

548.73:546.33

Dawton, Ralph H V M

1936.12.23. Intensities of X-ray reflections from single crystals of sodium between 120 and 370° K.

Proc. phys. Soc. Lond. **49**, 294–306 (1937).

551.51.053.5

Naismith, R

1937.01.13. **Ionospheric conditions during the solar eclipse of 19 June 1936.**

Proc. phys. Soc. Lond. **49**, 214–224 (1937).

621.385.3

Myers, D M

1936.07.24. **The division of primary electron current between grid and anode of a triode.**

Proc. phys. Soc. Lond. **49**, 264–278 (1937).

669.018:541.123.23

Jones, H

1936.12.16. **The phase boundaries** in binary alloys, Part 1: The equilibrium between liquid and solid phases.

Proc. phys. Soc. Lond. **49**, 243–249 (1937).

669.144.24:536.413.2

Owen, E A
Yates, E L

1937.01.06. **An X-ray** investigation of pure iron-nickel alloys, Part 3: The thermal expansion of alloys rich in iron.

Proc. phys. Soc. Lond. **49**, 307–314 (1937).

669.144.24:536.413.2

Owen, E A
Yates, E L
Sully, A H

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 5: The variation of thermal expansion with composition.

Proc. phys. Soc. Lond. **49**, 323–325 (1937).

669.144.24:548.712

Owen, E A
Yates, E L
Sully, A H

1937.01.06. **An X-ray investigation of pure iron-nickel alloys,** Part 4: The variation of lattice-parameter with composition.

Proc. phys. Soc. Lond. **49**, 315–322 (1937).

669.35:541.123.23

Jones, H

1936.12.16. **The phase boundaries** in binary alloys, Part 2: The theory of the α, β phase boundaries.

Proc. phys. Soc. Lond. **49**, 250–257 (1937).

669.355.1

Mott, N F

1936.12.16. **The energy of the superlattice in β brass.**

Proc. phys. Soc. Lond. **49,** 258–263 (1937).

669.791.5:538.22

Bates, L F
Tai, L C

1936.10.27. The magnetic properties of manganese amalgams.

Proc. phys. Soc. Lond. **49,** 230–236 (1937).

674.045:541.183.55

Barkas, Wilfred W

1936.12.15. Wood-water relationships, Part III. Molecular sorption of water by Sitka spruce wood.

Proc. phys. Soc. Lond. **49,** 237–242 (1937).

AUTHOR INDEX

674.045:541.183.55

Barkas, Wilfred W

1936.12.15. Wood-water relationships, Part III. Molecular sorption of water by Sitka spruce wood.

Proc. phys. Soc. Lond. **49,** 237–242 (1937).

669.791.5:538.22

Bates, L F
Tai, L C

1936.10.27. The magnetic properties of manganese amalgams.

Proc. phys. Soc. Lond. **49,** 230–236 (1937).

546.217:533.16

Bond, W N

1936.05.14. The viscosity of air.

Proc. phys. Soc. Lond. **49,** 205–213 (1937).

536.491

Buckley, H

1936.08.12. Note on the radiation between two coaxial radiating cylinders.

Proc. phys. Soc. Lond. **49,** 225–229 (1937).

548.73:546.33

Dawton, Ralph H V M

1936.12.23. Intensities of X-ray reflections from single crystals of sodium between 120 and 370° K.

Proc. phys. Soc. Lond. **49,** 294–306 (1937).

669.018:541.123.23

Jones, H

1936.12.16. **The phase boundaries in binary alloys, Part 1: The equilibrium between liquid and solid phases.**

Proc. phys. Soc. Lond. **49**, 243–249 (1937).

669.35:541.123.23

Jones, H

1936.12.16. **The phase boundaries in binary alloys, Part 2: The theory of the α, β phase boundaries.**

Proc. phys. Soc. Lond. **49**, 250–257 (1937).

669.355.1

Mott, N F

1936.12.16. The energy of the superlattice in β brass.

Proc. phys. Soc. Lond. **49**, 258–263 (1937).

621.385.3

Myers, D M

1936.07.24. The division of primary electron current between grid and anode of a triode.

Proc. phys. Soc. Lond. **49**, 264–278 (1937).

551.51.053.5

Naismith, R

1937.01.13. Ionospheric conditions during the solar eclipse of 19 June 1936.

Proc. phys. Soc. Lond. **49**, 214–224 (1937).

669.144.24:536.413.2

Owen, E A
Yates, E L

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 3: The thermal expansion of alloys rich in iron.

Proc. phys. Soc. Lond. **49**, 307–314 (1937).

669.144.24:548.712

Owen, E A
Yates, E L
Sully, A H

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 4: The variation of lattice-parameter with composition.

Proc. phys. Soc. Lond. **49**, 315–322 (1937).

669.144.24:536.413.2

Owen, E A
Yates, E L
Sully, A H

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 5: The variation of thermal expansion with composition.

Proc. phys. Soc. Lond. **49**, 323–325 (1937).

539.23

Quarrell, A G

1937.01.22. Structural changes during the growth of metal films.

Proc. phys. Soc. Lond. **49**, 279–293 (1937).

669.144.24:548.712

Sully, A H
Owen, E A
Yates, E L

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 4: The variation of lattice-parameter with composition.

Proc. phys. Soc. Lond. **49**, 315–322 (1937).

669.144.24:536.413.2

Sully, A H
Owen, E A
Yates, E L

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 5: The variation of thermal expansion with composition.

Proc. phys. Soc. Lond. **49**, 323–325 (1937).

669.791.5:538.22

Tai, L C
Bates, L F

1936.10.27. The magnetic properties of manganese amalgams.

Proc. phys. Soc. Lond. **49**, 230–236 (1937).

669.144.24:536.413.2

Yates, E L
Owen, E A

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 3: The thermal expansion of alloys rich in iron.

Proc. phys. Soc. Lond. **49**, 307–314 (1937).

669.144.24:548.712

Yates, E L
Sully, A H
Owen, E A

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 4: The variation of lattice-parameter with composition.

Proc. phys. Soc. Lond. **49**, 315–322 (1937).

669.144.24:536.413.2

Yates, E L
Sully, A H
Owen, E A

1937.01.06. An X-ray investigation of pure iron-nickel alloys, Part 5: The variation of thermal expansion with composition.

Proc. phys. Soc. Lond. **49**, 323–325 (1937).

ADDENDA

SUBJECT INDEX

539.231:537.311.31

Lovell, A C B

1936.11.05. The electrical conductivity of thin films of the alkali metals spontaneously deposited on glass surfaces.

Proc. phys. Soc. Lond. **49**, 89–94 (1937).

539.231:546.682

Cosslett, V E

1936.11.01. The structure and electrical conductivity of thin films of indium.

Proc. phys. Soc. Lond. **49**, 121–133 (1937).

Saturation-discrimination for F. H. G. P. and W. D. W.

Wave-length λ (μ.)	Saturation-discrimination, $\log \frac{L_W+L_S}{L_S}$	
	F. H. G. P.	W. D. W.
0·47	1·77	1·48
0·48	1·55	1·32
0·49	1·40	1·22
0·50	1·26	1·15
0·51	1·14	1·09
0·52	1·05	1·04
0·53	0·98	0·98
0·54	0·93	0·92
0·55	0·86	0·83
0·56	0·73	0·72
0·57	0·55	0·58
0·58	0·92	0·75
0·59	1·09	1·02
0·60	1·18	1·21
0·61	1·25	1·35
0·62	1·29	1·43
0·63	1·34	1·51
0·64	1·36	1·57
0·65	1·40	1·62

REFERENCES

(1) WRIGHT, W. D. and PITT, F. H. G. *Proc. phys. Soc.* **47**, 205 (1935).

(2) NELSON, J. H., page 332 of this volume.

(3) MARTIN, L. C., WARBURTON, F. L. and MORGAN, W. J. *Spec. Rep. Ser. Med. Res. Coun., Lond.*, No. 188 (1933).

THE COLOUR-VISION CHARACTERISTICS OF A TRICHROMAT, PART 2

By J. H. NELSON, A.R.C.S., D.I.C., B.Sc.

Received 21 *October* 1936. *Read* 28 *May* 1937

ABSTRACT. The author's luminosity curve, trichromatic coefficients, mixture curves, complementary wave-lengths and their mixture in terms of luminosity, and the hue- and saturation-discrimination curves have been obtained and the results tabulated.

In a recent paper by Wright and Pitt(1) the importance of having the complete characteristics of individual observers was pointed out, and they gave the data for their own eyes. In this paper the characteristics of the present author, also a trichromat, are given. The apparatus used for the measurements was the Wright colorimeter, which has been fully described elsewhere(2).

The methods of expressing the results have been dealt with previously, and it is only necessary to repeat them very briefly. The trichromatic coefficients are expressed on the W. D. W. system, in which the primaries are red 0·65 μ., green 0·53 μ. and blue 0·46 μ., and the units are based on two monochromatic matches at 0·5825 μ. and 0·4940 μ. The luminosity is referred to an equal-energy spectrum, the maximum being taken as unity.

The position of the maximum of the luminosity curve for the observer J. H. N. is 0·552 μ., which compares with 0·558 μ. for W. D. W., 0·562 μ. for F. H. G. P., and 0·555 μ. for the standard observer. The position of the standard illuminant B in the colour triangle for the observer J. H. N. lies farther towards the yellow than the normal; this is the reverse of what holds for the observers W. D. W. and F. H. G. P. This indicates a slightly more dense macular pigment than the normal, a conclusion which is further supported by the luminosity curve, which shows a lower luminosity in the blue than those of either W. D. W., F. H. G. P. or the normal.

The complementary wave-lengths have been calculated from the colour triangle, together with the proportions, in luminosity, in which they should be mixed to give the standard illuminant B.

The hue-discrimination for the observer J. H. N. is similar to that for the previous two observers, showing a secondary minimum in the violet, and not in the red.

As has been pointed out by Wright and Pitt, since the saturation-discrimination does not vary very much when measured from the spectral locus, it would be instructive to know the variation of the saturation-discrimination when measured from the white point; the requisite data were therefore obtained by adding a small

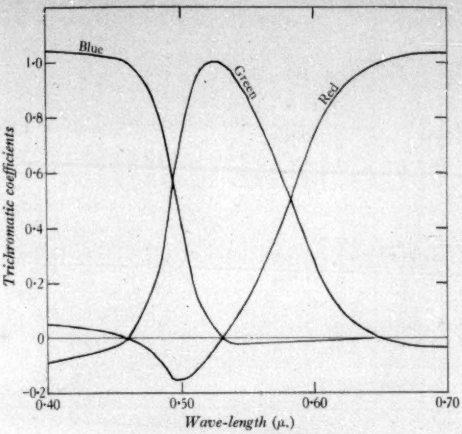


Figure 1. Spectral coefficients.

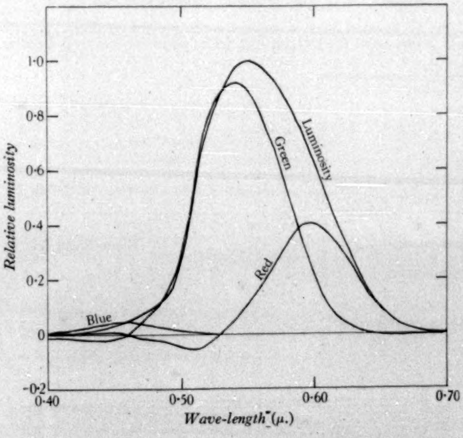


Figure 2. Equal-energy luminosity and spectral mixture curves.

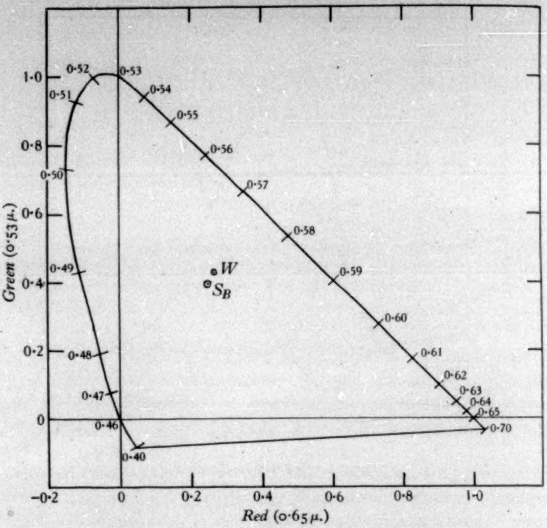
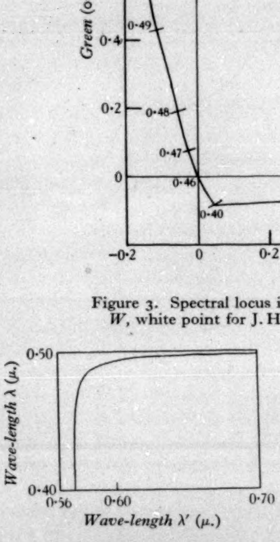


Figure 3. Spectral locus in colour triangle plotted on W. D. W. system. *W*, white point for J. H. N. S_B, white point for standard observer.



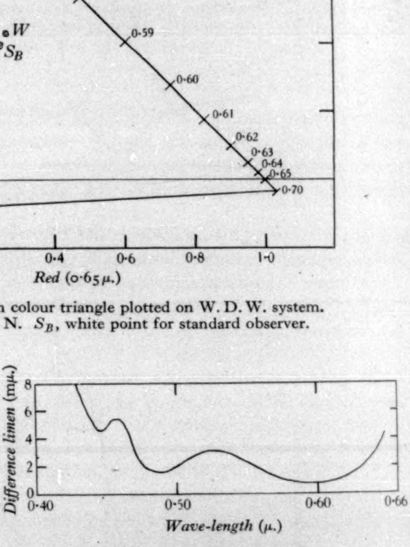


Figure 4. Complementary wave-lengths.

Figure 5. Hue-discrimination.

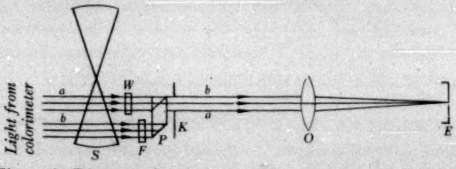

Light from colorimeter
a
b
W
b
a
K
F
P
S
O
E

Figure 6. Diagram of optical system for saturation-discrimination.

Wave-length λ (μ.)	Relative lumino-sity of equal-energy spectrum	Trichromatic coefficients			Mixture curves for equal-energy spectrum			Complementary wave-lengths (μ.)		Lumino-sity of λ to be mixed with unit lumino-sity of λ′	Hue-dis-crimina-tion; just-noticeable wave-length differences (μ.)	Saturation-discrimi-nation, $\log \frac{L_W+L_S}{L_S}$	Wave-length λ (μ.)
		B (0·46μ.)	G (0·53μ.)	R (0·65μ.)	L_B	L_G	L_R	λ	λ′				
0·40	0·0007	1·043	−0·093	0·050	0·0052	−0·0095	0·0038	—	—	—	—	—	0·40
0·41	0·0028	1·038	−0·081	0·043	0·0098	−0·0113	0·0043	0·41	0·5710	0·01006	—	—	0·41
0·42	0·0070	1·033	−0·069	0·036	0·0165	−0·156	0·0061	0·42	0·5712	0·0132	—	—	0·42
0·43	0·0125	1·028	−0·057	0·029	0·025	−0·020	0·0075	0·43	0·5715	0·0164	0·0080	—	0·43
0·44	0·0196	1·023	−0·046	0·023	0·0325	−0·0202	0·0073	0·44	0·5718	0·0195	0·0054	—	0·44
0·45	0·0270	1·018	−0·035	0·017	0·0404	−0·0204	0·007	0·45	0·5722	0·0227	0·0048	—	0·45
0·46	0·0468	1·000	0·000	0·000	0·0468	0·000	0·000	0·46	0·5729	0·0345	0·0054	—	0·46
0·47	0·075	0·951	0·076	−0·027	0·039	0·051	−0·015	0·47	0·5750	0·0676	0·0032	—	0·47
0·48	0·109	0·862	0·194	−0·056	0·030	0·099	−0·020	0·48	0·5780	0·137	0·0018	1·125	0·48
0·49	0·150	0·683	0·430	−0·113	0·018	0·162	−0·031	0·49	0·5894	0·386	0·0016	1·08	0·49
0·50	0·274	0·412	0·736	−0·148	0·012	0·306	−0·044	—	—	—	0·0021	1·04	0·50
0·51	0·528	0·190	0·930	−0·121	0·008	0·575	−0·055	—	—	—	0·0027	0·995	0·51
0·52	0·763	0·070	0·998	−0·068	0·004	0·797	−0·038	—	—	—	0·0031	0·96	0·52
0·53	0·890	0·000	1·000	0·000	0·000	0·890	0·000	—	—	—	0·00315	0·916	0·53
0·54	0·973	−0·020	0·945	0·075	0·000	0·921	0·052	—	—	—	0·0029	0·85	0·54
0·55	0·998	−0·019	0·868	0·151	0·000	0·888	0·110	—	—	—	0·0024	0·78	0·55
0·56	0·978	−0·018	0·776	0·242	0·000	0·801	0·177	—	—	—	0·0018	0·65	0·56
0·57	0·928	−0·014	0·664	0·350	0·000	0·677	0·249	—	—	—	0·00135	0·475	0·57
0·58	0·850	−0·008	0·534	0·474	0·000	0·515	0·335	0·4838	0·58	0·204	0·00105	0·76	0·58
0·59	0·753	−0·007	0·404	0·603	0·000	0·356	0·397	0·4909	0·59	0·428	0·0009	0·93	0·59
0·60	0·625	−0·007	0·277	0·730	0·000	0·221	0·404	0·4940	0·60	0·707	0·0008	1·03	0·60
0·61	0·491	−0·006	0·178	0·828	0·000	0·114	0·377	0·4958	0·61	0·983	0·0009	1·150	0·61
0·62	0·371	−0·006	0·101	0·905	0·000	0·051	0·320	0·4967	0·62	1·18	0·0012	1·245	0·62
0·63	0·261	−0·004	0·052	0·952	0·000	0·019	0·242	0·4973	0·63	1·33	0·0018	1·33	0·63
0·64	0·173	−0·002	0·022	0·980	0·000	0·005	0·168	0·4975	0·64	1·42	0·0028	1·435	0·64
0·65	0·094	0·000	0·000	1·000	0·000	0·000	0·094	0·4976	0·65	1·51	0·0044	1·485	0·65
0·66	0·048	0·000	−0·022	1·022	0·000	−0·001	0·049	—	—	—	—	1·54	0·66
0·67	0·023	0·000	−0·030	1·030	0·000	−0·0009	0·0239	—	—	—	—	1·62	0·67
0·68	0·013	0·000	−0·031	1·031	0·000	−0·0008	0·0138	—	—	—	—	1·66	0·68
0·69	0·0085	0·000	−0·032	1·032	0·000	−0·0005	0·0090	—	—	—	—	1·72	0·69
0·70	0·0059	0·000	−0·033	1·033	0·000	−0·00028	0·00618	0·4979	0·70	1·62	—	1·75	0·70
1931 C.I.E. source S_B		0·307	0·431	0·262	Relative luminosities of trichromatic units of primaries								
λ=0·4940μ.		0·572	0·572	−0·144	0·46μ.	0·53μ.	0·65μ.						
λ=0·5825μ.		−0·008	0·504	0·504	0·068	1·000	0·711						

quantity of spectral colour to white (standard illuminant B). For this purpose it was necessary to make some additions to the apparatus, the optical system necessary in addition to the colorimeter being shown in figure 6. A brass sector *S*, coated with magnesium oxide, is illuminated by the light from a lamp as specified by the C.I.E. (1931) for standard illuminant B[(3)]. The sector is arranged so that both halves of the photometric field in the prism *P* are filled with white light during one half of the revolution, and that during the other half of the revolution a monochromatic radiation of known wave-length is admitted to the top half of the field, forming beam *b*. This monochromatic radiation is obtained from the spectrum supplying the instrument primaries, and the intensity is controlled by a calibrated photometer wedge. The intensity of the white in the top half of the field (beam *b*) may be controlled by neutral filters *F*, but it is advisable to use only the lightest filters as the darker ones may deviate somewhat from neutrality. In the lower half of the field the intensity of the white forming beam *a* is controlled by a very shallow photometer wedge. The sector is arranged to run at two speeds. The fast speed is fast enough to remove flicker and thus provide two uniform fields, a white *a* and a white-plus-monochromatic *b*, between which a saturation step may be made. At the slow speed the intensities of the white and the monochromatic radiation can be compared by means of flicker.

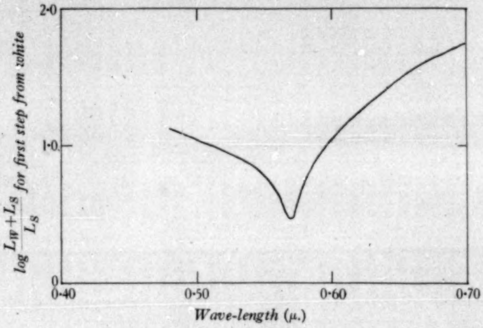


Figure 7. Saturation-discrimination.

When the observations are being taken the sector is first run slowly, and the observer is asked to equate the intensities of the white and the monochromatic radiation by adjusting the intensity of the latter so that flicker may be removed. The sector is then run fast, and the observer is asked to adjust the intensity of the monochromatic radiation until he can just notice a difference in colour between the top and bottom halves of the field, the intensities of both halves being kept the same by adjusting the intensity of the white of the bottom half of the field. In this way the intensity of monochromatic radiation to be added to the white to make one step can be found. If L_W is the intensity of the white and L_S that of the added monochromatic radiation, then the saturation step can be expressed as the logarithm of the ratio $(L_W+L_S)/L_S$. When this fraction is large, only a small quantity of monochromatic radiation is needed to cause a just noticeable change in colour.

The measurements of saturation-discrimination taken by this method may be compared with the results obtained by Martin, Warburton and Morgan(4). The curve given in the present paper falls below that given by them in the blue-green region, but its general shape is the same.

The author wishes to thank Dr W. D. Wright for his help, and the Medical Research Council for their financial assistance.

REFERENCES

(1) Wright, W. D. and Pitt, F. H. G. *Proc. phys. Soc.* **47**, 205 (1935).
(2) Wright, W. D. *Trans. opt. Soc.*, Lond., **29**, 225 (1927–8).
(3) Smith, T. and Guild, J. *Trans. opt. Soc.*, Lond., **33**, 73 (1931–2).
(4) Martin, L. C., Warburton, F. L. and Morgan, W. J. *Spec. Rep. Ser. Med. Res. Coun.*, Lond., No. 188 (1933).

DISCUSSION

Mr J. Guild. Papers of this kind, giving full details of the colour-vision of individual observers, are of great value. One of the main difficulties in correlating the data on colour-vision accumulated in the past has been due to the fact that the various functions—visibility, colour-matching, hue-discrimination, etc.—have usually been determined by different people using different apparatus and standards. From the point of view of providing knowledge of the visual processes it is much more important to have comprehensive information about a few people than to have a little information about many people. If the programme followed at the Imperial College provides us with one or two more individual studies of this kind it will be of great value. I note that the evidence of this paper and of the former paper by Wright and Pitt goes to show that the wave-length of maximum visibility is on that side of the value $0{\cdot}555\,\mu$. of the C.I.E. standard visibility function which corresponds to the departure from normality in macular pigmentation, as is indicated by the position of the white point on Dr Wright's form of the colour diagram. This confirms that the standard value must be fairly nearly correct for normal observers, despite the fact that this view has recently been called in question.

THE EFFECT OF SECONDARY BETA RADIATION ON GAMMA-RAY MEASUREMENTS MADE IN AIR

By C. W. WILSON, M.Sc., Physics Dept., Westminster Hospital Annexe, London

Received 6 *January* 1937. *Read* 12 *March* 1937

ABSTRACT. A sensitive method of measuring small ionization currents is described, and the effect of secondary beta radiation upon ionization measurements of gamma radiation is examined. It is shown that if ionization chambers made of light-atom materials have walls less than 4·0 mm. thick, secondary beta radiation is recorded so that readings are in excess of the true values. The results explain some discrepancies found by other workers.

§ 1. INTRODUCTION

For the evaluation of the gamma-ray dosage in experiments on the biological effects of gamma radiation it is often necessary to make ionization measurements in air at small distances from radium sources. The literature shows that measurements made in air in the vicinity of radium sources may give values that differ widely from what might have been expected. Spear and Grimmett⁽¹⁾ for example found that the intensity-values due to a one-gramme radium source were consistently 24 per cent higher than the values obtained by calculation. They measured the intensities in air at distances of from 3 to 8 cm. from the radium with condenser chambers of the Sievert pattern⁽²⁾ which were constructed of elektron metal and had walls 1·0 mm. thick. Similarly Benner⁽³⁾ found that for distances of from 3 to 14 mm. from a radium source, the intensity-values measured in air with ionization chambers having walls of elektron metal and brass respectively, of thickness 0·3 mm., were always considerably (14 per cent or more) in excess of those calculated.

The purpose of this paper is to describe some experiments which show that the discrepancies referred to can be ascribed to secondary beta radiation from the metal filters of the radium sources. If the chamber wall is sufficiently thin such radiation can enter the air volume of the chamber and add considerably to the ionization produced by gamma radiation. On the other hand, if the wall be thickened by the necessary amount no secondary beta radiation will be recorded.

§ 2. APPARATUS AND METHODS

The ionization chamber and current-measuring system that formed the main part of the apparatus are shown diagrammatically in figure 1. The ionization chamber was of the thimble type and made of elektron metal with a wall 0·5 mm.

thick. Its air volume was 1·31 cm.^{3} The lead from the graphite inner electrode of the chamber is carried to the Lindemann electrometer on a number of polished amber buttons through an air-tight brass tube that is continuously evacuated to avoid ionization losses. The tube also serves as an earthed screen for the lead.

For measuring ionization currents a null method is used, the potential across the capacity *C* being continuously increased to maintain the needle of the instrument at earth potential. The processes of isolating and earthing the electrometer needle start and stop the stop watch incorporated in the circuit, figure 1, so that the time taken for a measured change of potential is automatically recorded. If ionization currents are to be compared, the potential-change per second is a suitable measure. If the capacity *C* is known an absolute determination of the current can be made. Thus with a graphite ionization chamber the apparatus serves as an X-ray dosemeter. This, in fact, is its routine use. The auxiliary circuit *A*, figure 1, is solely for the purpose of providing an easy control upon the sensitivity and zero setting of the electrometer$^{(4)}$.

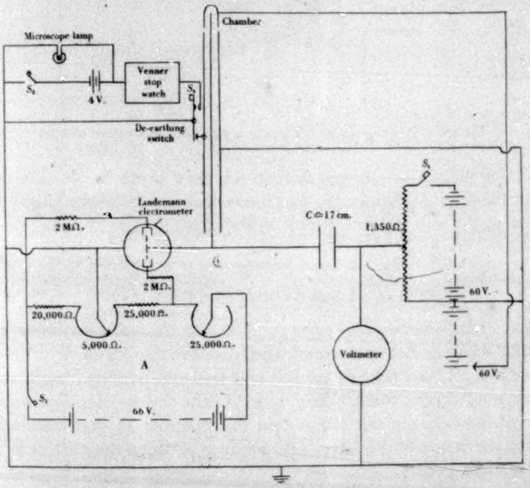


Figure 1. Arrangement for measuring ionization currents.

The construction and mounting of the ionization chamber is shown in figure 2, which also illustrates how the radiation source was set up relative to the chamber. The lead to the electrode is carried through an amber plug which is highly polished and waxed into the brass tube to form an air-tight joint. The thimble fits tightly over the shoulder on the amber plug. The source of gamma rays consists of radon in glass capillaries which are contained in a platinum tube with a wall 0·5 mm. thick.

The latter is sufficient to absorb all primary beta radiation. In all the experiments the source and ionization chamber were arranged parallel to one another and the source was mounted in a holder attached to the evacuated lead. Thus, if any movement of the lead and its chamber occurred, the distance between the source and the chamber did not change.

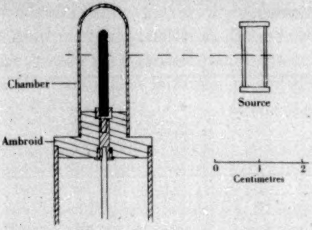


Figure 2. Dispositions of ionization chamber and radon source.

A series of sheaths of various thicknesses were made in elektron metal to fit tightly over the original chamber so that the wall-thickness of the chamber could be increased from 0·5 mm. up to 6·0 mm. as required.

§ 3. EXPERIMENTS

The effect of large metal filters upon the ionization recorded in chambers with walls of various thicknesses. For this experiment two circular metal discs were used as secondary filters. These were of copper and lead respectively. Each was 5·0 cm. in diameter and 0·5 mm. thick. When added to the arrangement shown in figure 2 they were placed between the source and the chamber so that the source was in contact with the centre of the filter. The distance between the centres of the source and chamber was 3·0 cm.

A series of measurements of the ionization current were made under three sets of conditions, (*a*) with no extra filter present, (*b*) with the copper filter added and (*c*) with the lead filter added. For each set of conditions readings were taken for different thicknesses of the wall of the chamber. Alternate records were taken in order to allow for decay of the radon source during the period of the experiment. Figure 3 shows the results expressed in graphical form.

It is seen that when the chamber wall is only 0·5 mm. thick the introduction of the metal filter causes the ionization to increase very markedly in spite of the absorption of gamma radiation that must occur. This increase is about 19 per cent for the copper sheet and as much as 32 per cent for the sheet of lead.

Two distinct types of results are obtained according to whether the large secondary filters are included or not. When no filter is added the ionization in the chamber increases with increase in wall-thickness up to a maximum value when the wall is about 2 mm. thick, after which a slow fall takes place. When either the copper or lead filter is included, the ionization decreases continuously with increasing wall-thickness. Such a result as the latter is to be explained in terms of a strong secondary beta radiation from the filters, which augments the ionization for the smallest wall-thickness and is progressively absorbed as the wall-thickness is increased. Finally the results obtained with the filters present are lower than those with no filter, in consequence of absorption of the primary gamma rays in the filters. The preliminary rise in the curve expressing the results with no filter added is due to extra ionization by recoil electrons liberated from the thickened wall of the chamber. This question has received considerable attention from Mayneord and Roberts (5).

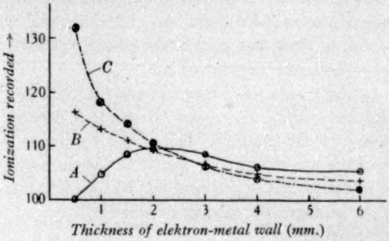


Figure 3. Showing how the current in an ionization chamber is affected by secondary radiation from a metal filter. *A*, no filter included; *B*, copper filter included; *C*, lead filter included.

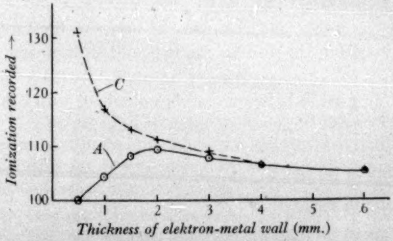


Figure 4. Showing the elimination of the effects of secondary beta radiation by increasing the wall-thickness of the ionization chamber. *A*, no filter included; *C*, lead filter included.

As is to be expected from the work of Stahel (6), the amount of secondary beta radiation liberated from the lead sheet is very much greater than that from the copper sheet.

The wall-thickness that absorbs all secondary beta radiations from metal filters. In this experiment the same lead filter was used as before but a hole was cut at its centre having exactly the shape and size of the platinum tube that contained the radon source. Thus when the filter was placed in position as in the first experiment no absorption of primary gamma radiation occurred in it. The distance between the source and ionization chamber was 3·0 cm. as before.

Measurements were made of the ionization current within the chamber with and without the filter for the range of wall-thicknesses 0·5 mm. to 6·0 mm.; the results obtained are expressed graphically in figure 4. It is seen that when the chamber wall has a thickness of 4·0 mm. or more, the ionization recorded is not changed by the addition of the filter. Thus all secondary beta radiation is absorbed in the wall of the ionization chamber if its thickness is 4·0 mm. or more. Therefore any ionization chamber of light-atom material that is used for measuring gamma radiation in air is liable to record secondary beta radiation from nearby metal parts if its walls are not at least 4·0 mm. thick.

It seems then that the excess values found by Spear and Grimmett(1) were due to the fact that their ionization chambers had elektron metal walls only 1·0 mm. thick, while a large disc of brass was used as the primary radium filter. To confirm this result a further experiment was carried out.

Comparison of readings made with thin-walled and thick-walled ionization chambers when the large brass disc used by Spear and Grimmett is present. The actual brass filter, 10 cm. in diameter and 2·3 mm. thick, used by Spear and Grimmett was available, and an aperture was cut in it in exactly the same manner as in the case of the lead sheet used in the second experiment. It was therefore possible to add this in the same way to the arrangement already described (figure 2) without absorbing any primary gamma radiation.

Readings were made of the ionization currents with and without the brass disc in position, an elektron-metal ionization chamber with walls (*a*) 1·0 mm. thick and (*b*) 4·0 mm. thick being used. The results are summarized in the table for various distances between the source and chamber, in terms of the ratio of the readings obtained with and without the disc for the two wall-thicknesses.

Table. Comparison between readings obtained with thin-walled and thick-walled ionization chambers

Distance between source and ionization chamber	Ionization with brass disc / ionization with no brass disc	
	1·0-mm. wall	4·0-mm. wall
2·24 cm.	1·083	1·000
3·00 ,,	1·105	1·012
3·96 ,,	1·130	0·985
5·08 ,,	1·140	1·000
6·03 ,,	1·162	1·008
7·00 ,,	1·144	1·004

These results show that when the wall of the ionization chamber is only 1·0 mm. thick, the brass disc adds from 8 to 16 per cent to the ionization recorded, whereas if the wall is 4·0 mm. thick the presence of the brass does not affect the result within the experimental error. In the experiments of Spear and Grimmett the disc would serve as an even more efficient radiator, since the radium was spaced round a circle 8·0 cm. in diameter so that more of the metal surface was exposed to its action.

§4. DISCUSSION OF RESULTS

If satisfactory measurements of gamma radiation are to be made in air with ionization chambers of light-atom materials in the vicinity of radium sources, the walls of the chamber must be at least 4·0 mm. thick in order to avoid excess ionization by secondary beta radiation. It would therefore appear to be impracticable to make reliable measurements of gamma radiation at distances less than 4·0 mm. from a radium source. It is very likely that the calculated values of intensity given by Spear and Grimmett⁽¹⁾ are more nearly correct than those obtained by measurement.

§5. ACKNOWLEDGEMENTS

The author wishes to acknowledge his indebtedness to Mr N. H. Pierce for his assistance with the experiments, and to the British Empire Cancer Campaign whose financial support has helped make it possible to carry out the work.

REFERENCES

(1) Spear, F. G. and Grimmett, L. G. *Brit. J. Radiol.* **8**, 231 (1935).
(2) Sievert, R. M. *Acta Radiol.*, Stockh., Supplementum **14** (1932).
(3) Benner, S. *Acta Radiol.*, Stockh., **15**, 85, p. 291 (1934).
(4) Grimmett, L. G. *Proc. phys. Soc.* **45**, 117 (1933).
(5) Mayneord, W. V. and Roberts, J. *Brit. J. Radiol.* **7**, 158 (1934).
(6) Stahel, E. *Strahlentherapie*, **44**, 575 (1932).

DISCUSSION

Mr W. Binks. It is now well known that in order to measure gamma radiation by an ionization method, the walls of the measuring-chamber should be thick enough to prevent extraneous primary and secondary beta radiation from entering the air cavity—that is to say, the thickness of the chamber-wall should not be less than the range of the fastest beta particles in the material of which the wall is composed. In this connexion I would like to draw the author's attention to a number of papers published in recent years by Friedrich, Schulze and Zimmer, Glasser, Mayneord and Roberts and by Kaye and myself. In the case of chambers having walls thinner than the beta-ray range the ionometric conditions are somewhat complex, the measured ionization depending upon the particular experimental arrangement adopted. For example, it seems to depend not only on the material and thickness of the filter but on the latter's position—that is, on whether the filter is near the radium or near the chamber. Further, it depends on the size and shape of the source and chamber and on the distance between them.

The observations of Friedrich and Schulze (1935) on the effects of different filters (0·1 mm. platinum, 0·3 mm. platinum plus 1·5 mm. brass, and 6·6 mm. lead) would appear to contradict those of Mr Wilson, but it should be noted that the sources and chambers and their distances apart were different in the two cases. Thus the ionization measured by means of chambers having too thin walls is dependent upon the distribution of the primary and secondary beta radiation at the location of the chamber, the curves shown by Mr Wilson representing a particular example of this phenomenon.

I agree with the author that it would be impracticable to make reliable measurements of gamma radiation at distances from the source less than the range of the beta particles. But it would seem that when considering the biological effect of the radiations from radium one ought to take into account the beta radiation as well as the gamma radiation received by the tissue. In certain locations, for instance in the case of tissue adjacent to a radium needle or that of the superficial layers of tissue of a patient who is irradiated from an external radium source, the secondary beta radiation has an important bearing on the total energy absorbed by the tissue. It is doubtful, therefore, whether the calculated gamma-ray intensities at distances less than 4 mm. from a radium source give even an approximate idea of the actual energy absorbed. For these distances it would be better to use ionization chambers of appropriate wall-thickness.

AUTHOR'S reply. I was quite aware of the fact that other workers had dealt with the problem of secondary beta radiation, but it was just this particular example of the phenomenon with which I was concerned. The work done by Spear and Grimmett was carried out in this laboratory, and since it dealt with an important biological effect that occurred for a specific gamma-ray intensity, it was essential to know the value of the latter. The experiments I have described seem to show which of the intensity-values published by Spear and Grimmett was correct, and for this reason they appeared to be worth recording.

ON THE OPTICAL CONSTANTS OF ALLOYS OF THE COPPER-ZINC SYSTEM

By H. LOWERY, Ph.D., D.Sc., F.Inst.P., Principal of the North-Western Polytechnic, London; H. WILKINSON, M.Sc.Tech., and D. L. SMARE, M.Sc.Tech., College of Technology, Manchester

Received 13 *February* 1937. *Read* 9 *April* 1937

ABSTRACT. Values of the optical constants (refractive index, reflection coefficient and absorption coefficient) are given for some alloys of the copper-zinc system (α, β and γ brass) over the range λ 4358 to λ 6800, as determined by the method of Drude. Curves showing the variation in the optical constants with composition for particular wave-lengths of light are also shown.

§ 1. INTRODUCTION

In continuation of an experimental investigation on the optical constants of some simple binary alloys$^{(1)}$, the present paper is concerned with dispersion-measurements in the visible region of the spectrum for the copper-zinc system.

This system is interesting from an experimental point of view on account of the extension of the absorption band of copper into the visible, resulting in the very distinct colour-variation in alloys in the α phase. From the red of pure copper the colour changes gradually to the typical yellow of brass at the end of the α phase (39 per cent by weight of zinc). The narrow β phase (46·5 to 49·6 per cent of zinc) again shows the red of copper, and from 60 to 69 per cent of zinc we have the extremely hard, brittle, silvery γ phase.

Measurements of the optical constants of alloys in each of these three phases have been made, though the main part of the work has been concerned with the α phase. An attempt has been made to obtain dispersion curves over the range λ 4358 to λ 6800 for a number of specimens of varying composition, and to obtain curves showing the variation in the optical constants with composition for particular wave-lengths of light.

§ 2. EXPERIMENTAL DETAILS

The general arrangements of the apparatus and method used, essentially that of Drude, have been fully described in previous papers. A parallel beam of light, plane-polarized at an azimuth of 45° to the vertical, is incident at an angle θ on a polished specimen of the alloy mounted vertically. The reflected elliptically polarized light is analysed by a Soleil-Babinet compensator, measuring the phase-difference Δ between the horizontal and vertical components of the beam, and an analysing Nicol prism fitted with a half shade to measure the azimuth ψ of the restored plane-polarized light.

From the measured quantities θ, Δ and ψ the refractive index n and the absorption coefficient K are calculated from the following equations, due to Drude:

$$\begin{aligned} \tan Q &= \sin\Delta \tan 2\psi, \\ \cos 2P &= \cos\Delta \sin 2\psi, \\ S &= \sin\theta \tan\theta \tan P, \\ A &= S^2 \cos 2Q + \sin^2\theta = n^2 - K^2, \\ B &= S^2 \sin 2Q \qquad\quad = n^2 + K^2, \\ 2n^2 &= \sqrt{(A^2+B^2)} + A, \\ 2K^2 &= \sqrt{(A^2+B^2)} - A.^* \end{aligned}$$

The reflecting-power at normal incidence is given by

$$R = \frac{n^2+K^2+1-2n}{n^2+K^2+1+2n} \times 100 \text{ per cent.}$$

In view of the decay in the measured phase-difference Δ with exposure, corrections have been applied to this constant throughout the work in this paper. The corrections were applied to the compensator scale readings from observations taken at intervals during the experiments. All values of Δ given in the tables were calculated from these corrected compensator readings.

Preparation of the specimens. The copper specimens used were prepared from clean electrolytic copper, melted and allowed to solidify in vacuo. The brasses were prepared in air in an induction furnace. Electrolytic copper was first melted and the zinc, comprising B.D.H. zinc sticks As.T., was dropped into the melt in small pieces, each wrapped in paper to retard volatilization and ignition until the zinc was submerged. By using an excess of zinc to compensate for the loss in melting, alloys of approximately the desired compositions were obtained. The alloys cast cleanly into iron moulds and were quite free from pinholes.

Chemical analysis of the specimens gave the percentages by weight of copper shown in the table.

Composition of specimens

Specimen number Phase	1 α	2 α	3 α	4 α	5 α	6 β	7 γ	Extra specimen, α phase
Weight of copper (per cent)	93·42	91·09	87·60	80·60	74·61	52·85	32·75	86·12
Weight of zinc (per cent) by difference	6·58	8·91	12·40	19·40	25·39	47·15	67·25	13·88
Atomic percentage of zinc	6·42	8·67	11·92	18·98	24·85	46·45	66·63	13·56

---

* The imaginary dielectric constant ϵ occurring in dispersion theory of metals is written $\epsilon=(n-iK)^2$, where n and K are as above. Drude used $\epsilon=n^2(1-ik)^2$ so that his absorption coefficient $k=K/n$.

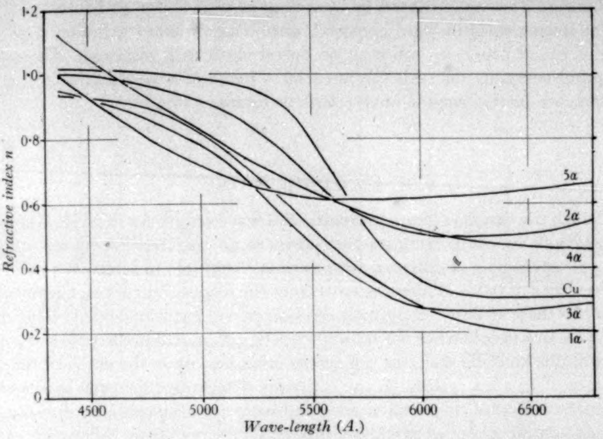


Figure 1.

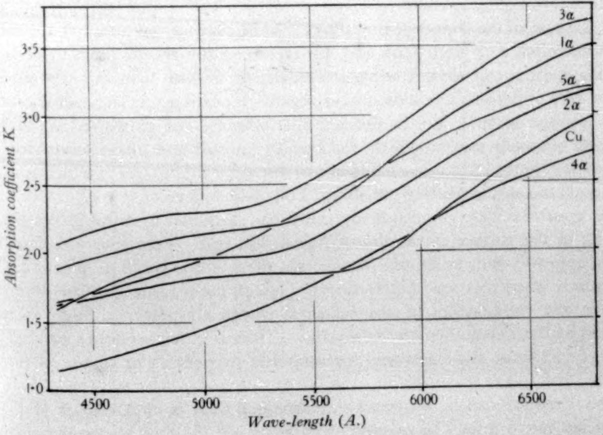


Figure 2.

Micrographic examination of the specimens revealed a cored structure in the α specimens. This was removed by annealing at 580° C. for 40 hours.

The mirror surfaces were prepared, after a preliminary grinding with a 0000 grade of emery paper, by polishing on Selvyt cloth with magnesia. The values of the optical constants for each specimen for a range of wave-lengths in the visible spectrum are plotted against wave-length in figures 1 to 4.

§ 3. DISCUSSION

Though the variation of the constants with wave-length for individual specimens yields smooth curves in every instance, there is no correlation between dispersion curves for specimens of different composition. Attempts to select, for given wave-lengths, series of values of the constants from the dispersion curves, figures 1 and 2, and to plot these against composition result in curves entirely devoid of any distinct form. This lack of coherence is a consequence of differences in the polished surfaces; results of this kind illustrate the difficulties attendant upon the study of the optical properties of an alloy system. If the constants determined for each specimen were truly characteristic of the metal or alloy and were not influenced by the state of the surface, a natural coherence would occur between the results for different specimens. Alternatively, a similar coherence would be obtained if a process of polishing could be devised to produce the same surface condition in each alloy, though the constants would not necessarily represent the optical properties of the undisturbed metallic structure; see figures 5 and 6.

In the case of the copper-nickel alloys (1) some success was attained in producing the same polish with each alloy and, by averaging the results from three separate polishes in order to even out minor irregularities, smooth {constants, composition} curves were obtained. The difficulty as regards repeating this successful procedure in the present instance lies in the fact that whereas the copper-nickel alloys are hard and relatively easy to polish, the brasses are soft and easily scratched; moreover, their colour makes it more difficult to discern a slight tarnish which sometimes appears on the surface during polishing. To polish a piece of copper or soft brass to a clear glass-like state of surface by the usual methods, avoiding excessive cold-working of the surface, is an almost impossible task. Very fine scratches nearly always appear(2) and, as Drude has shown, these are capable of polarizing light, particularly when they are unidirectional. Though the measured phase-difference Δ between the components of the reflected elliptically-polarized light is not influenced by these scratches, the azimuth ψ is increased for scratches parallel to the plane of incidence and decreased for scratches perpendicular to the plane of incidence.

This variation can be observed experimentally. It is of the order of 1°. Discrepancies due to it may be avoided by carrying out the final stages of polishing so as to avoid unidirectional scratches or by taking care always to mount the specimen with the predominating scratch-directions always the same.

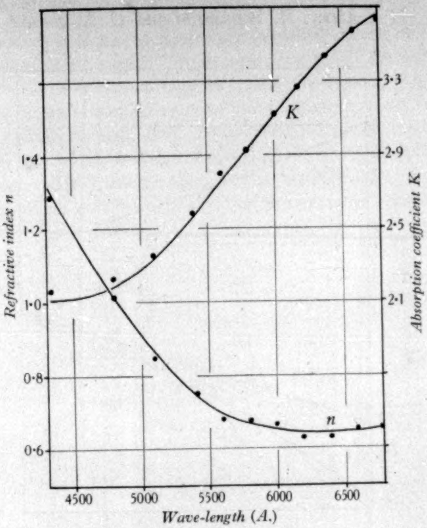


Figure 3. Specimen β brass.

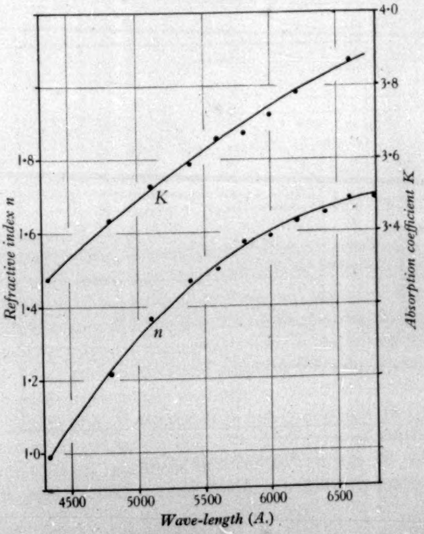


Figure 4. Specimen γ brass.

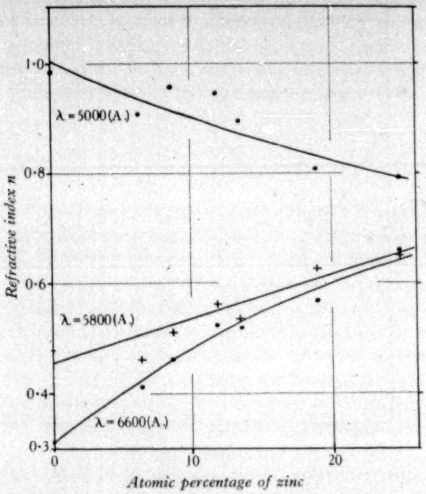


Figure 5.

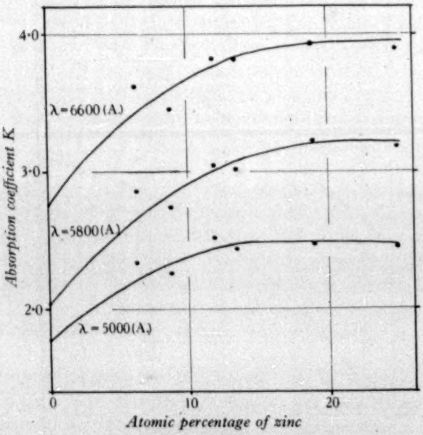


Figure 6.

The possibilities of using the electrolytic polishing process of Jacquet(3), which has proved successful for copper(4), were considered. Here again the position is not satisfactory. Though the method is quite feasible for brasses, it is more tedious in operation since the exact conditions of solution and current and voltage have to be determined separately for each alloy. Again, there is no reason to believe that these conditions, when correctly determined and applied, would effect the removal of the constituents of the alloy (made the anode in the process) in the proportions in which they happened to be present. Finally, the considerable variation found in the measured constants when different depths of the mechanically smooth disturbed surface are removed introduces the disadvantage of having to make an arbitrary choice of the depth of material to be removed, and this in turn entails much laborious work to ensure that the depth shall be the same in every instance.

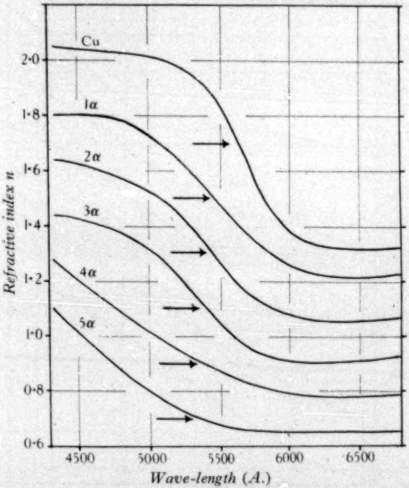


Figure 7. To obtain refractive indices from the graph the following corrections should be subtracted from the ordinates: 1·0 for copper, 0·8 for 1α, 0·6 for 2α, 0·4 for 3α, 0·2 for 4α, 0·0 for 5α. The arrow indicates the value 0·7 of n.

The method employed in the present work is that of embedding all the specimens in a lead block and grinding and polishing them simultaneously. This ensures that each one receives practically the same treatment as regards the amount of cold work sustained. Even so, however, it is hardly probable that alloys with slightly different mechanical properties will receive identical treatment, and the optical constants measured on specimens polished in this way do not give as smooth a curve when plotted against the zinc-content as might be expected for a variation of a physical constant produced by an increasing proportion of zinc in a solid solution. The variation of *n* and *K* with composition is shown in figures 5 and 6 for three wave-lengths, λ 6600, λ 5800 and λ 5000 A., for the alloys 1α, 2α, 3α, 4α, 5α, simultaneously polished in the lead block.

It is evident that the dispersion curves, figures 1 and 2, though showing an increasing divergence in form from the curves characteristic of copper as the zinc-content increases, require correction of the constants before any quantitative

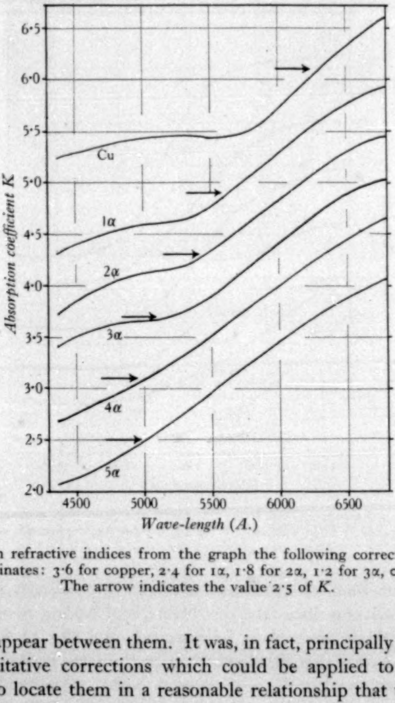


Figure 8. To obtain refractive indices from the graph the following corrections should be subtracted from the ordinates: 3·6 for copper, 2·4 for 1α, 1·8 for 2α, 1·2 for 3α, 0·6 for 4α, 0·0 for 5α. The arrow indicates the value 2·5 of *K*.

relationship will appear between them. It was, in fact, principally with the object of suggesting quantitative corrections which could be applied to these dispersion curves in order to locate them in a reasonable relationship that the change in the constants with composition was investigated.

Variations in optical constants due to differences in polish take the form of an approximately parallel shift of the dispersion curves to higher or lower values of the constants. Figures 7 and 8 show the dispersion curves for *n* and *K* after the curves for each alloy have been so shifted to such an extent that the values of the constants for the wave-lengths λ 6600, λ 5800 and λ 5000 A. now coincide with the values read off from the smooth curves drawn in figures 5 and 6 for the variation of the constants with composition.

It must be clearly understood that this arrangement of the results is not intended to do more than indicate the interrelationship between the constants of copper and the α brasses shown by our experiments. The values of the constants are correct values only in so far as the constants for the mechanically polished copper specimen may be assumed to be true values. That these may vary considerably upon repetition and with different polishing technique is well established and has been discussed more fully in a previous paper⁽⁴⁾.

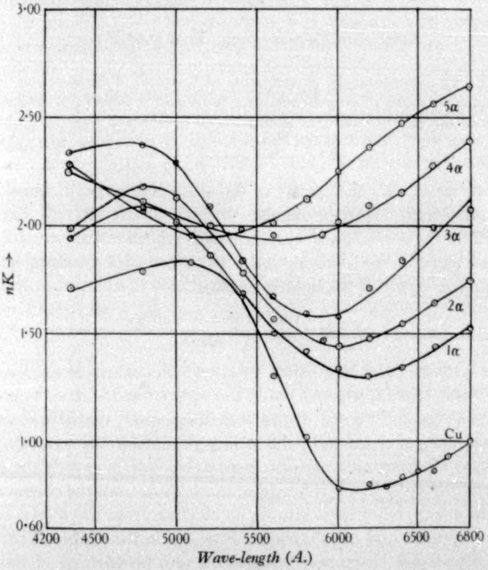


Figure 9.

REFERENCES

(1) Lowery, Bor and Wilkinson. *Phil. Mag.* **20**, 390 (1935).
(2) Drude. *Ann. Phys.*, Lpz., **39**, 481 (1890).
(3) Jacquet. *Trans. electrochem. Soc.* **69**, 629 (1936).
(4) Lowery, Wilkinson and Smare. *Phil. Mag.* **22**, 769 (1936).

THE THEORETICAL INTERPRETATION OF THE OPTICAL CONSTANTS OF COPPER-ZINC ALLOYS

By N. F. MOTT, M.A., F.R.S., H. H. Wills Physical Laboratory, University of Bristol

Received 13 *February* 1937. *Read* 9 *April* 1937

ABSTRACT. The results of the experiments of Lowery, Wilkinson and Smare on the optical constants of alloys of copper and zinc (α, β and γ brass) are discussed from the point of view of the electric theory of metals.

In this note we discuss the results of the preceding paper⁽¹⁾ from the point of view of the electric theory of metals.

If n, K are the optical constants, then nK is related to the rate of absorption of energy by the metal in the following way. If we consider a volume of metal $d\tau$ in which the electric vector of the light is E, then⁽²⁾

$$nK\nu d\tau = \frac{\text{rate of loss of energy}}{E^2}.$$

In figure 9 of the preceding paper are shown the values of nK for the copper-zinc alloys. Pure copper is seen to have an absorption band with its long wave-length limit between λ 5500 and λ 6000. It has been suggested⁽²⁾ that this absorption band is due to the ejection of electrons by the incident light from the 3*d* level of the copper atom. The type of electronic transition responsible is thus exactly the same as that which gives rise to X-ray absorption edges; as we know from the chemical behaviour of copper, the energy required to remove an electron from the *d* level is very small, so it is not surprising that the absorption edge lies in the visible. The fact that the absorption edge is not sharp may be ascribed to a broadening of the 3*d* level of the atom into a narrow band of levels in the crystal.

As zinc is added to copper, three effects may be noticed, as in figure 9 of the previous paper. (*a*) The absorption on the long wave-length side of the edge increases. (*b*) The absorption edge becomes less sharp. (*c*) The absorption edge is displaced in the direction of shorter wave-lengths.

Effect (*a*) can be ascribed simply to the increased resistance of the metal, which damps the induced vibrations of the electrons in the metal and so increases the absorption. We shall not attempt to calculate the absorption to be expected.

Effect (*b*) can be accounted for as follows. In order to find the energy $h\nu$ corresponding to the wave-length of the edge we have to calculate the work required to move an electron from the $3d$ level of one of the copper atoms to the conduction levels of the crystal. This is made up of two parts: (1) The work W_1 required to remove an electron from a d level of a copper atom right out of the crystal. (2) The work W_2 (*minus* the work function of the alloy) required to bring the electron back into the crystal. We consider first the term W_1. The picture of a copper-zinc alloy to which one is lead by the electron theory of metals is an array of ions Cu^+ and Zn^{++} embedded in a sea of negative charge. The negative charge tends to cluster round the zinc ions so that each copper atom has only a small excess negative charge and each zinc atom a small excess positive charge. These charges have been estimated from the resistivity(2) and from the energy of the superlattice(3) to be about $\Delta Q = \pm 0{\cdot}075e$, where e is the electronic charge. Now the electrostatic potential at any lattice point due to these charges will on the average be zero, because the copper and zinc atoms are distributed at random in the lattice. But the electrostatic potential at any copper atom which happens to have more zinc atoms as nearest neighbours than the average number will be higher than zero, and at those which have an excess of copper atoms as nearest neighbours it will be lower. The potential of any lattice point will fluctuate by an amount comparable with $\Delta Q/r_0$, r_0 being the interatomic distance. Thus the work required to remove an electron from the lattice will fluctuate by an amount of the order of magnitude $e\Delta Q/r_0$, which is approximately equal to $0{\cdot}075e^2/r_0$ or 0·4 eV. Since a wave-length λ 5500 corresponds to 2·2 eV. this is of the order of magnitude which is observed.

Effect (*c*). According to the electron theory of metals the kinetic energies of the electrons in a metal have values between 0 and a maximum energy $E_{\max}$ given by

$$E_{\max} = 36{\cdot}1\,(n_0/\Omega)^{\frac{2}{3}},$$

where Ω is the volume per atom in $\text{cm}^3 \times 10^{24}$ and n_0 the mean number of free electrons per atom. If an electron is added to the metal, it cannot have kinetic energy less than $E_{\max}$. Thus we may write for the work W_2 required to bring an electron back into the metal

$$W_2 = \text{a negative constant} + E_{\max}.$$

Now in a series of copper-zinc alloys, as the amount of zinc is increased n_0 increases much faster than Ω and so $E_{\max}$ increases. The values are as shown in table 1.

Table 1

Composition of alloy (Atoms per cent of zinc)	n_0	$E_{\max}$ (eV.)
0	1	6·98
20	1·2	7·70
40	1·4	8·33
50	1·5	8·61

Thus for an alloy containing 20 atoms per cent of zinc, the absorption edge will be shifted towards shorter wave-lengths by

$$7{\cdot}70 - 6{\cdot}98 = 0{\cdot}28 \text{ eV}.$$

Taking the wave-length of the edge for pure copper to be 6000 A., the theoretical values for the alloys shown in figure 9 of the preceding paper are as shown in table 2.

Table 2

Alloy	Composition (Atoms of zinc per cent)	Shift in the edge (eV.)	Absorption edge (calculated)
1α	6·42	0·2	λ 5500
2α	8·67	0·3	5250
3α	11·92	0·4	5000
4α	18·98	0·6	4640
5α	24·85	0·8	4300

The displacements of the edge are rather greater than those observed; the latter are however difficult to estimate, owing to the broadening of the edge discussed above.

REFERENCES

(1) Lowery, Wilkinson and Smare. P. 345 of this volume.

(2) Mott and Jones. *Theory of the Properties of Metals and Alloys*, pp. 107, 119, 294 (Oxford, 1936).

(3) Mott. P. 258 of this volume.

SENSITIVITY VARIATION OF X-RAY PHOTOGRAPHIC FILMS

By Wm. H. GEORGE, M.Sc., Ph.D., F.Inst.P., University of Sheffield

Received 14 *November* 1936. *Read in title* 9 *April* 1937

ABSTRACT. An experimental study of the variation of sensitivity from place to place on an X-ray photographic film has been made, so that fluctuations of blackening, due to intensity-variation of the incident radiation, can be distinguished from those due to film sensitivity. Double-film exposures are made with the two sensitive surfaces in contact, and the processing is carried out in a simple mechanical apparatus so that the films move always with accelerated motion relative to the liquids. It is found that if X-ray photographic films are used with the technique described and are blackened until they transmit about half the incident light, then the variations of sensitivity are such as may lead to maximum deviations in the individual measurements of X-ray intensity of the order ±6 per cent in single-film exposures or of ±3 per cent in double-film exposures. The mean deviations are of the order ±2 per cent.

§ 1. INTRODUCTION

The results of the experiments here described relate to the following problem. If a piece of X-ray film exposed in a uniform beam of X rays is then processed (i.e. treated) under prescribed conditions, to what degree of accuracy will adjacent regions of the film be uniformly blackened?

Although the problem arose out of some work on the interaction of polarized X rays and crystals(1), the results are applicable also to X-ray crystallography with tiny single crystals giving small spots in rotation and oscillation photographs, or to fine spectral lines in powder photographs.

§ 2. EXPERIMENTS

Uniform exposure. The object of the work is, in the measurement of a fluctuating X-ray intensity, to differentiate between the X-ray fluctuations and those due to the photographic materials and processes. Since an X-ray beam cannot be directly observed by the coincidence method, the uniformity of the beam cannot be directly judged. In any very sensitive laboratory method of measuring X-ray intensity, the final observations, consisting of deflections of some measuring instrument, may fluctuate about a mean value but are never constant when the ionization chamber or other detecting apparatus is moved across the beam of X rays. It is therefore necessary to define in terms of observable quantities what part of the fluctuations of blackening of a film are to be ascribed to variations of intensity of the incident beam.

Two facts help in formulating the definition Firstly, it is found that the time average of intensity at some distance from an X-ray tube is free from rapid fluctuations in adjacent tiny areas (say 1 × 0·2 mm.). Secondly, the absorption of X rays in photographic film is so slight that the beam transmitted through one film is still sufficiently intense to blacken a second film placed behind and in contact with the first film. Hence if two films are exposed in contact and at some distance from an X-ray tube, any difference between the ratio of blackening of two areas on the first film and the corresponding ratio on the second film will be ascribed to variation in the film-sensitivity. The mean blackening for the two areas will be fixed by using the first fact in the way explained in § 3.

All the experiments were therefore carried out by exposing simultaneously pairs of films in contact. The camera is shown in figure 1. The two films, protected from light by black paper, rest behind two lead screens pierced at front and back by a slit *S* exposing a suitable area of film and allowing the X-ray beam to pass through this part of the camera and its support at the back. The time *t* of exposure necessary to blacken a film until it transmitted only half of the light incident normally upon it in a microphotometer was first determined. The camera was then loaded with a pair of experimental films and set upon its geometrical supports *A*, *B*, *C*. When the X-ray tube was running steadily, two exposures were made, each for a period of a little more than $\frac{1}{2}t$. During the first period the camera was fixed in the position shown in figure 1, and during the second it was reversed about a vertical axis through *A*. The slit therefore remained in the same position relative to the X-ray tube but during the second period the beam passed through the films in the reverse direction. The exposure for each film was therefore $\frac{1}{2}t$ in the direct beam and $\frac{1}{2}t$ in a beam which had first penetrated the other film. The same region of the beam was used in each period for the same part of each film.

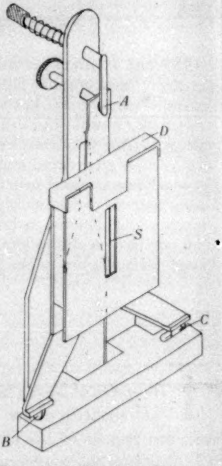


Figure 1. Diagram of camera. *S*, slits; *A*, *B*, *C*, geometrical constraints; *D*, lead cap.

For intensity-calibration the films were then removed from the camera and a rotating-sector exposure was made in another camera upon a part of the unexposed surface.

A filament X-ray tube with copper anticathode and nickel filter was used in all the experiments.

Uniform development. Uniform development as usually defined seems to be inapplicable to experimental work when different parts of a film are exposed in a uniform beam for different times, or when they are exposed in a non-uniform beam for the same time or in fact in any circumstances resulting in non-uniform blackening. Suppose that developer kept at constant temperature and concentration is directed on to such a film in a rapid uniform stream. The developing chemicals will diffuse into the gelatin and react with the affected silver-halide grains, producing various reaction products which diffuse outwards into the stream of fresh developer. Within the film the rate of blackening will depend upon the concentration of developing chemicals, and upon the diffusion rates of their replacement and of the removal of reaction products. These constants are beyond the experimenter's control. In much optical photography, including sound-recording on film, only a thin layer on the upper surface of the emulsion is affected by the radiation, but in the present experiments the absorption of the X rays is so slight that the whole depth of the exposed regions contains developable grains. The chemicals must therefore diffuse through thicker regions than in optical photography. According to common supposition the diffusion must take place also through a layer of liquid adhering to the surface of film in contact with the moving liquid.

Because difficulties arising from the grain and associated with extra background fog, a film which is to be measured on a microphotometer is not developed to gamma infinity. If, therefore, adjacent patches of the film have first been subject to different exposures, it follows that during development they will not be in contact, *within* the film, with the same concentration of developing chemicals for the same time. In this sense then uniform development is impracticable. Since experimental research is concerned with the accessible rather than with the inaccessible it is more helpful here to choose some other definition of uniform development.

Instead of the arbitrarily chosen theoretical definition of uniform development an arbitrarily chosen definition based on the experimenter's actions(2) will be used. Accordingly a film will be said to be subject to uniform development when, at constant temperature, its whole surface has been immersed throughout in rapidly flowing developer of constant composition or in violently stirred developer whose composition is changed only by the progress of the development reactions. A method by which these conditions may be fulfilled for a fairly large film, coated with emulsion on one side and blackened optically, is described elsewhere(3), together with a survey of many other methods. There is considerable difficulty in using the method for X-ray films measuring only 3 × 2 cm. and coated on both sides with emulsion. After trial of a number of different methods the simple apparatus shown in figure 2 was devised; it was found to give self-consistent results.

Processing. The two films are firmly clamped side by side vertically in a detachable framework *F* made of ebonite and stainless steel. The glass tank *T* and the block *B* are removable, but the rest of the apparatus, consisting of reciprocating mechanism, reduction pulleys and electric motor, is screwed to the bench. To avoid delay in making the necessary changes, a separate tank is used for each liquid. When the loaded frame is fixed in position the dry films are quickly plunged into developer by raising the tank, and the reciprocating mechanism is started. This gives 140 complete vibrations per minute, each of total displacement 2 cm.

The films always move with accelerated motion relative to the solutions. This was relied upon to help the interchange of liquids at the film surface. To change the surrounding liquid, a propeller from a toy motor boat was rotated in front of the oscillating films. As the results obtained with and without the use of the propeller appeared to be the same, it was later discarded. The agitation of the liquid was studied by two methods. The first was with coffee grounds, washed and decanted several times to remove all turbidity. These showed the large-scale agitation to be very thorough and free from dead regions. Secondly the regions near the film were examined in close detail by using dye introduced through a fine jet. The removal of liquid introduced as close to the film as possible and the dispersal throughout the bulk of liquid were too rapid to be followed by eye. In all the experiments splashing and the introduction of air bubbles, which accelerate oxidization of the developer, were avoided by adjusting the depth of liquid in the tank.

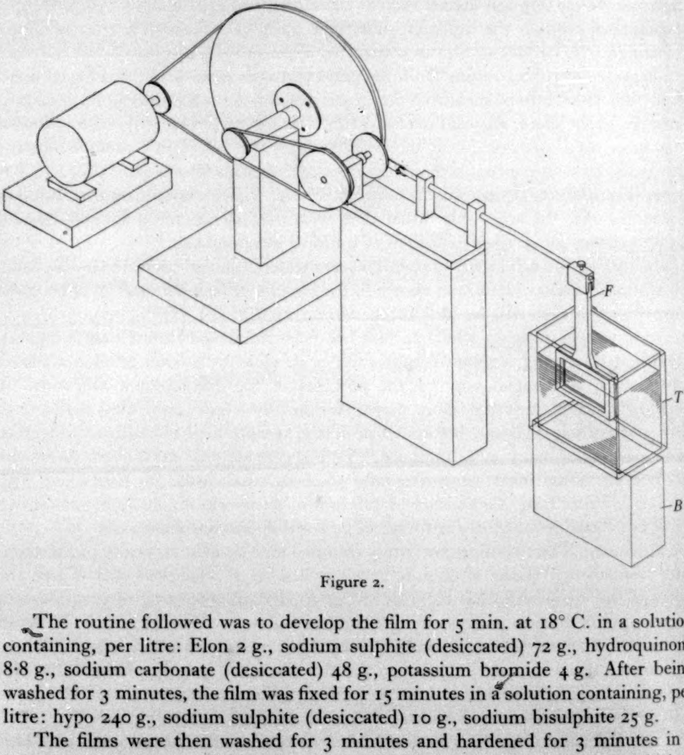


Figure 2.

The routine followed was to develop the film for 5 min. at 18° C. in a solution containing, per litre: Elon 2 g., sodium sulphite (desiccated) 72 g., hydroquinone 8·8 g., sodium carbonate (desiccated) 48 g., potassium bromide 4 g. After being washed for 3 minutes, the film was fixed for 15 minutes in a solution containing, per litre: hypo 240 g., sodium sulphite (desiccated) 10 g., sodium bisulphite 25 g.

The films were then washed for 3 minutes and hardened for 3 minutes in a solution containing, per litre, 10 cm. of formalin (40 per cent formaldehyde solution) and 5 g. of desiccated sodium carbonate. Next, the frame was removed from the oscillator and the films were washed in running water for from 1½ to 2 hours. From time to time the frame was agitated in the water to remove the bubbles which collect on the film surfaces even when rapidly flowing water is used. When the washing was completed, viscose sponge was used to remove as much water as possible from the films which were then dried slowly in a horizontal position at room temperature. Filtered solutions were used throughout to avoid scratching of the film surfaces by particles thrown against them by the rapidly moving liquids.

Microphotometry. The dry films were measured with a Moll microphotometer(4, 5). To ensure that the galvanometer deflections should be, as far as possible, unaffected by deviation of light out of the optic plane containing the thermopile slit, owing to scratches, the viscose sponging of the film was always done in a direction perpendicular to that of its subsequent passage through the microphotometer.

Each instantaneous galvanometer deflection was the result of exploring a region of the film measuring 1 × 0·033 mm.

§ 3. RESULTS

On account of the graininess of the film, the record of galvanometer deflections taken on the microphotometer drum *D* appears as a line subject to many sudden inflections. Each record was therefore divided into strips 5 mm. wide, from which the readings plotted in the two typical pairs of graphs, figure 3, were obtained as follows. The films were exposed in pairs and each half of the figure represents the results got from one pair. Points got from measurements of one film of the pair are joined by solid lines. Broken lines are used to join the points relating to the other film of the pair. A straight line was drawn through each portion of the whole curve contained in each 5-mm. strip of the paper record got from the microphotometer drum, so as to divide its curve into two parts lying equally above and below the straight line. The galvanometer deflection corresponding to the mid-point of this

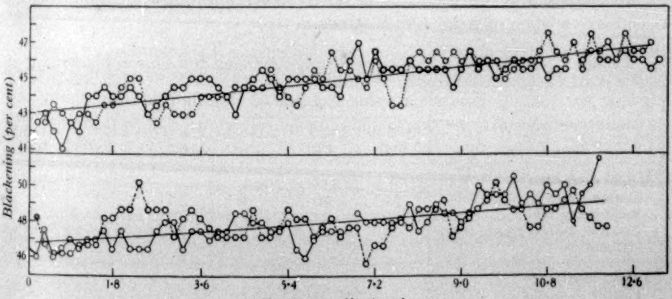


Figure 3.

line was taken as the average of the whole 5-mm. strip. To avoid possible error due to prejudice, strips adjacent to the one studied were hidden from view.

The measurements were expressed in terms of the blackening *B* defined as follows:

$$B = \frac{\text{galvanometer deflection due to strip of blackened film}}{\text{galvanometer deflection due to clear film}} \times 100;$$

with this definition the blackening of an opaque film would be 100 per cent, of a clear film zero, and of a film transmitting one-half of the light incident normally upon it 50 per cent. Each point on the graphs corresponds to a strip 5 mm. wide on the drum record *D* or to a region measuring 1 × 0·18 mm. on the X-ray film. Since the double exposure of each pair of films was made without disturbing the films in their holder, the regions of each in contact could be determined by the distance from a shadow cast by a lead screen behind which part of each film was protected from the X rays. Each unit of displacement on the horizontal axis of figure 3 represents a displacement of 0·18 mm. on the film.

Each of the straight lines, later taken as representing the blackening due to the X-ray intensity to be measured, was got from a mean curve passing through the algebraic mean of each pair of points, one from the solid and one from the dotted curve. For the upper diagram the seventy points of this mean curve were then divided into sets of ten adjacent points and the algebraic mean of each set was used to give one point. The method of least squares was used to draw the straight line through the six points. In the lower diagram the points were grouped into seven sets of eleven each.

An analysis of the deviations of the observations from this derived mean due to sensitivity variation of X-ray film is shown in table 1.

Table 1. Numbers of points representing deviation from mean blackening

	Limits of variation (per cent)					
	±(0 to 0·5)	±(0·5 to 1·0)	±(1·0 to 1·5)	±(1·5 to 2·0)	±(2·0 to 2·5)	±(2·5 to 3·0)
Upper diagram:						
Dotted curve (i)	39	22	6	1	1	—
Solid curve (ii)	36	25	6	3	—	—
Mean of paired points from (i) and (ii)	47	20	2	—	—	—
Lower diagram:						
Dotted curve (i)	35	21	6	2	1	—
Solid curve (ii)	31	17	10	6	1	1
Mean of paired points from (i) and (ii)	41	20	4	—	—	—

The use of simpler methods of processing the films, such as developing in a rocking dish, or stroking with cotton-wool under the liquids or rotating in a flask of liquid, gave fluctuations much greater than those shown in table 1, and the results were too inconsistent to justify their being reported. The results given in figure 3 are typical provided the technique described in this paper is used. When it was found that the method gave self-consistent results, further experiments were discontinued. To establish which parts of the technique may be omitted without affecting the results an elaborate series of control experiments of the cause-and-effect type would be necessary.

The following conditions apply to all the results reported. The exposures were made with general radiation from an X-ray tube with a copper anticathode and a nickel filter. The photographic density of the exposures was about 0·301; the area of blackening was about 1 × 12 mm.; the individual mean measurements relate to tiny strips 1 × 0·18 mm. From rotating sector photographs it was found that under these conditions a variation of blackening of 1 per cent corresponds to a change of X-ray intensity of 2 per cent. The variations of sensitivity are summarized in table 2.

Table 2. Percentage deviation from mean blackening (50 per cent) or density (0·3)

	Single-film exposure	Double-film exposure
Maximum departure by single measurements from mean blackening (per cent)	Blackening 3 X-ray intensity 6	Blackening 1·5 X-ray intensity 3
Percentage of measurements showing this maximum departure	1	4
Percentage of measurements lying between 49·5 per cent and 50·5 per cent	50	65
Percentage of measurements lying between 50·5 per cent and 51 per cent or between 49 per cent and 49·5 per cent	30	30

From this summary it is evident that with the use of the technique described, the variations of sensitivity of X-ray film are such as may lead to maximum deviations in the individual measurements of X-ray intensities of the order ± 6 per cent in single-film exposures or of ± 3 per cent in double-film exposures. The mean deviations are of the order ± 2 per cent.

§ 4. ACKNOWLEDGEMENTS

The work was carried out during my tenure of the Royal Society Sorby Fellowship and I wish to thank Prof. S. R. Milner, F.R.S., for laboratory facilities and the Royal Society and the Department of Scientific and Industrial Research for financial aid. Very generous help in materials, advice and the use of unpublished results was obtained from the Kodak Research Laboratory through the kindness of Mr E. R. Davies.

REFERENCES

(1) George. *Proc. roy. Soc.* A, **156**, 96–107 (1936).
(2) George. *Scientist in Action*, pp. 96–7 and 285 (1936). Williams and Norgate.
(3) Crabtree. *J. Soc. Mot. Pict. Engrs*, **25**, 512–22 (1935).
(4) Moll. *Proc. phys. Soc.* **33**, 207 (1921).
(5) Ornstein, Moll and Burger. *Objektive Spektralphotometrie* (1932). Braunschweig: Vieweg.

RAPID VARIATIONS IN THE MAGNETIC FIELD PRODUCED BY LIGHTNING DISCHARGES

By PROFESSOR HARALD NORINDER, Ph.D.

Communicated from the Institute of High Tension Research of
The University of Uppsala

Received 19 *February* 1937. *Read in title* 9 *April* 1937

ABSTRACT. Measurements of the rapid variations in the magnetic field produced by lightning discharges have been made by means of a frame aerial and a cathode-ray oscillograph. The observations made it possible under certain conditions to calculate the current-variations in lightning discharges, and maximal values up to 100 kA. were derived. These were in good agreement with results obtained by other indirect methods. Conclusions as to the structure of the current-variations in lightning discharges were drawn from the measurements.

---

§ 1. INTRODUCTION

FOR several years investigations have been carried out at Husbyborg, near Uppsala, in connexion with the electric properties of thunderstorms, and especially of the discharge characteristics of lightning. In the preliminary stages the work comprised measurements of the slow variation of the electrostatic field in thunderstorms. After some time the main interest turned to investigation of the rapid variations of the electromagnetic field produced by lightning discharges. Experiments in the first place were concentrated on the rapid variations of the electric field. Researches on this subject were especially desirable in regard to an important practical interest—the surges caused on high-tension transmission lines by lightning discharges.

With regard to such a practical application our investigations were in their first stage supported by the Royal Swedish Board of Waterfalls, an enterprise which is responsible for the high-tension transmission lines belonging to the State. A laboratory for surge phenomena and allied high-tension problems was consequently erected at Husbyborg. This laboratory became in 1932 incorporated with a newly erected research institute, which belonged to the University of Uppsala. The new institute had a special scientific purpose, being mainly devoted to the problems of high tensions, electric discharges in the atmosphere, and allied phenomena.

Researches on lightning discharges were thus obviously of special importance to the new institute, and the earlier investigations of the rapid variations in the electric field caused by lightning were continued. The results have been published elsewhere(1). The relations between the variations in the electric field caused by lightning and radio atmospherics were analysed also(2). In addition to these problems we have been occupied with an investigation of the rapid variations in the magnetic field caused by lightning discharges. The main purpose in this undertaking was to analyse the discharge variation of lightning, with special reference to the structure of the currents in the lightning paths. During the season of 1936 the experiments were continued, and improved recording methods, as compared with earlier investigations(3), were used. A considerable amount of new data was collected and it will be the purpose of this paper to give an account of the researches and their main results.

§ 2. THE METHODS OF RECORDING

The measuring instrument. Earlier and preliminary experiments which indicated that the variations within a lightning flash are very rapid enabled us to decide upon the most suitable methods for recording lightning discharges. The total time of discharge in a lightning flash is, on the other hand, rather slow and very often exceeds several hundredths of a second in duration. A lightning discharge was found to be built up of sequences of individual discharges, which sometimes comprised time intervals as small as a few tenths of a microsecond. For instance an individual examination of the slope of the front of the pulse in such partial discharges required an accuracy of measurement of some tenths of a μsec. From this it was evident that the only instrument which could be used with any hope of success must be a cathode-ray oscillograph. Further, it was found that the time variations were so rapid that a cathode-ray tube of the sealed type had not a sufficiently high recording-velocity. Hence it was necessary to use an oscillograph in which the film was placed in a vacuum and directly bombarded by the electron beam from the cathode.

During the experiments a special difficulty arose. When the oscillograph was in operation to record a lightning discharge it was not possible to obtain beforehand any indication of the moment of occurrence of the discharge. Thus a lightning flash with a duration of e.g. 0·001 sec. would require an exposure time of the film up to 10 min. or more. The film in an ordinary oscillograph with such a length of exposure would be much over-exposed, and no rapid transient phenomena could be recorded or recognized on such a film.

A means of avoiding these difficulties would be an electron-tube relay, which would operate by the lightning discharge. The arrangement should operate so that the electron beam of the oscillograph had to be directed into a recording position by means of the relay. The discharge variation of a lightning flash showed, however, such complicated variation forms that the relay would necessarily be very complicated. It was further not very advisable to introduce in the observation circuit a relay with a more or less pronounced time lag. Such an arrangement would, for instance, necessitate propagation of the complicated discharge variation in a delay cable during the time necessary to operate the relay.

It was evident, from the very beginning, that the problem had to be solved in such a manner that the electron beam of the oscillograph itself should be made to function as a relay. By this method a special advantage was gained, which was most useful in the recording of the complicated forms of variation in lightning discharges. With the relay the measuring circuit became very simple and easy to operate.

The principle which throughout has been used in the records of lightning discharges is illustrated in figure 1. The operation of the relay was as follows. When the plates 3, 5 have no voltage, the electron beam will pass from the cathode through the anode-hole between the plates 3 and against the target 4, which has such a position and dimensions that its shadow covers the central hole of the screen 6. A voltage variation derived from the potentiometer 9 and impressed upon the plates 3, 5 will bend the electron beam around the target, and by the cross-coupled system 5 the beam will be bent back and will pass through the hole 6. The plates 7 provide the time base from a circuit with either sinusoidal or linear time variation. The cathode-ray beam will thus fall upon the recording film only during the passage of the impulse, so that the target produces a characteristic zero line or band shadow in the oscillograms. This can be seen in the records here reproduced. In the majority of cases there is no difficulty in interpolating to determine the path of the beam across the zero band.

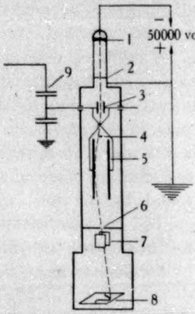


Figure 1. Relay of cathode-ray oscillograph. 1, cathode; 2, anode; 3, 5, deflection plates; 4, target; 6, screen with a central hole; 7, deflection plates for time circuit; 8, record film; 9, potentiometer.

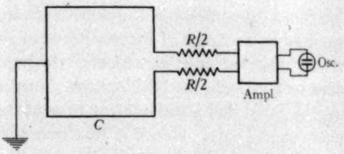


Figure 2. Frame aerial with connexions.

The relay method described by the author$^{(4)}$ has been used in various experiments in which the purpose was to record impulses whose time of arrival was not known beforehand. Typical of such unexpected impulses are lightning surges on transmission lines, impulses in radio antenna circuits, and atmospherics arriving from long distances. The method proved also to be very convenient in the recording of the rapid variations in the magnetic field.

The cathode-ray oscillograph constructed by the author and used in these experiments was of the cold-cathode type. The instrument is built of metal with the exception of the glass tube between the cathode and the anode.

The oscillograph contains a film-holder of such construction that the film can be moved to an exposure position from outside. It is possible to make up to 100 exposures without opening the oscillograph. The large number of exposures necessitated loading the film-holder with rolls of film of a length up to 10 metres. Such long films required a very safe and effective system of evacuation. The operation of the oscillographs had to be carried out in movable field stations without any supply of cooling-water. It was thus very inconvenient to use diffusion pumps. A mechanical molecular pump with a conical rotor was therefore constructed for the experiments. The use of a conical rotor had the advantage that the distance between the rotor and the cams between the spiral groove could easily be adjusted to give a very small clearance. The small distance allowed of a very high pump efficiency with as low a rotation speed as 3000 rev./min.

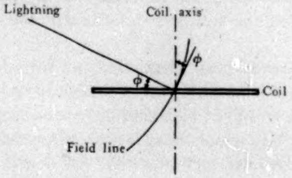


Figure 3. Orientation of coil to lightning path.

During the experiments it often happened that the time between lightning discharges was many minutes. The relay arrangement described did not fully prevent fogging of the film. After an exposure of some minutes it was necessary to shift to a fresh film-surface and thus it was possible that the supply of film in an oscillograph would be totally exposed during thunderstorms of a long duration. In order to avoid such a situation two oscillographs were simultaneously in operation. Both were charged with film and evacuated before the beginning of the observations. During the observation periods one instrument was used for the record and the other for indication by direct observation. The records were shifted over to the oscillograph used for indication when the film-supply of the first recording instrument was consumed, and the instrument with exposed film was subsequently used for indication. This alternation of the instruments was very useful and allowed of very long and undisturbed periods of operation.

§ 3. EXTERNAL EXPERIMENTAL ARRANGEMENTS

Frame aerials of special construction were found to be most suitable for measuring the rapid variation of the magnetic field. Certain precautions were necessary with regard to the winding and the dimensions of the coils; thus it was impossible to use coils with compact turns on account of pronounced disturbances arising in such a case between consecutive turns. It was necessary to separate the wire of each turn by an air distance of at least 2 cm. The coils showed with certain types of discharge-variations a tendency to become the seat of resonant oscillations, which were eliminated by suitable damping resistances.

In our first experiments the ends of the coil were directly connected to the deflection system of the oscillograph. In such a case the dimensions of the coils were to some extent determined by the voltage-sensitivity of the oscillograph. With a distance between the observation station and the lightning path of from 2 to 5 km. we received voltage-variations up to 800 V., which was more than sufficient for a record on the instrument. The coils used in such a case had a turn-surface of $1{\cdot}95 \times 10^7$ turns per cm.^{2} and the wire consisted of copper with a diameter of 1 mm. The connexion of the coil to the oscillograph was symmetrical and the mid-point of the coils was earthed as is illustrated in figure 2. The damping resistance R was 6000 Ω.

Direct control of the oscillograph from the coil was inconvenient as the limited sensitivity only permitted the stronger variations of the magnetic field to be recorded.

Therefore, as has already been mentioned, we introduced during the experiments of the summer 1936 an essential improvement in which the voltage-variations of the frame aerials were amplified by means of a special arrangement. Between the end of the coil and the oscillograph was placed a voltage-amplifier with an amplification up to 800 times. A necessary condition was that this amplifier should work without distortion within the range of variation in the observations. Further, the arrangement had the advantage that smaller amplitude-variations in the field could be recorded, and we received thus more extensive experimental data. The dimensions of the frame aerials were also considerably diminished by the introduction of an amplifier. The coils in the earlier arrangement had a surface of 130 m.^{2}, the coils of the new arrangement had a surface of only 12 m.^{2} In the latter case the small dimensions made it possible to use a coil which could easily be turned around a vertical axis. The large coils used in our earlier experiments necessitated, on the other hand, two separate coils mounted in two vertical planes at right angles.

§ 4. THE PRINCIPLE OF THE MEASUREMENTS

The observation of the magnetic-field variations was carried out by using the well-known induced effect of the magnetic fields on frame aerials. We introduce the following symbols: H is the horizontal component of the field in c.g.s. units, A is the surface of the frame in cm.^{2}, n is its turn number, V is the induced voltage in volts, and ϕ is in relation to figure 3 the angle between the coil and the direction of the lightning. The relation (1) will be as follows:

$$V = nA\frac{dH}{dt}\,10^{-8}\cos\phi \qquad \ldots\ldots(1).$$

It is obvious that the horizontal component of the field force H can be calculated from equation (1) by integration, and

$$H = \frac{10^8}{nA\cos\phi}\int V\,dt \qquad \ldots\ldots(2).$$

The values of H in what follows have been calculated from this relation.

§ 5. THE CALCULATION OF THE LIGHTNING CURRENTS

Calculation of the current-variation in a lightning flash from the variation of the magnetic field would require a knowledge of the manner in which the magnetic field varied with the distance from the path of the lightning. The ideal solution of this problem would have been to use simultaneous observations from stations situated at suitable distances from the path. Such a method would allow of a determination of the magnetic moment of the lightning discharges; it has not yet been used, however, because we found it to be too expensive since it involved duplication of the experimental arrangements.

Under certain conditions, as has already been shown in my earlier publication on lightning currents, it was possible to use an approximation method in the calculation of the current variations. The calculations were restricted to vertical lightning paths and the following relation was used:

$$I = 10\,V\,\frac{H\sqrt{(r^2+h^2)}}{h} \qquad \ldots\ldots(3),$$

where I is the current in the lightning path, H the horizontal component of the magnetic field, r the distance of the lightning path from the observation station and h the mean vertical length of the lightning path. For this mean height we have taken a value of 2·5 km. This was a plausible mean value in accordance with other observations which we have carried out on such heights. The amplification of the coil voltages resulted in an increase of several kilometres in the distance between the observation point and the lightning path. The uncertainty of ±0·5 km. in the height of the lightning path will for such longer distances cause an error in the calculated current-values of about ±12 per cent. The errors are smoothed out in the extended series of observations given in this paper.

The displacement currents may influence the determinations of the current-values of the lightning path, especially for the longer distances and to an extent, for the most disadvantageous cases, which has been estimated at 10 per cent. We have further supposed that the magnetic field lines will follow in concentric circles around the lightning path. Topographic conditions can in this respect provoke certain local disturbances. In our case no such disturbances have influenced the results. We estimate the total probable errors in the calculated values of the lightning currents under the most unfavourable conditions to be 20 to 22 per cent. Such errors must on the other hand be smoothed out to a great extent in an extended series of observations. As will be seen from what follows, the individual values of the maximum lightning currents change from a thousand to a hundred thousand amperes, and an error in the individual determinations will thus not be of any appreciable importance when we consider the problem as a whole.

§ 6. OBSERVATIONS

When a thunderstorm passed near the observation station and was suitably located for the production of a record, the frame aerial was directed in accordance with the most probable direction of the lightning paths. One or two observers noted the actual paths of the lightning with reference to their azimuthal positions and to previously determined markings on the horizon. The method provided a sufficiently accurate determination of the direction of the lightning tracks. These were also noted as carefully as possible as regards their angular size and general aspect. The distance to the flash was determined by the time difference between lightning and thunder.

A calculation of the maximum current-variation could be carried out only for vertical lightning flashes. A more limited analysis, however, of discharge characteristics, for instance the time sequences of consecutive partial discharges, and the total duration of lightning discharges were taken also from lightning paths inclined to the vertical or observed to be horizontal.

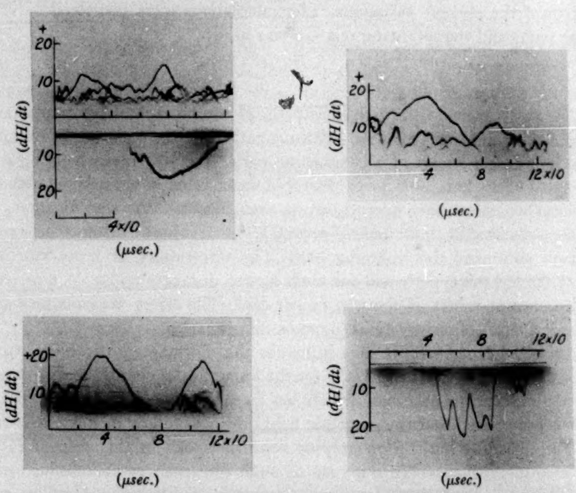


Figure 4. Oscillogram taken with frame aerial, with rapid base time.

Earlier experiments relating to the rapid variations of the electric field caused by lightning proved that, with few exceptions, an ordinary discharge visible as lightning is composed of consecutive partial discharges. The total duration reached values up to a hundredth part of a second. The partial discharges were on the other hand sometimes as short as only 10 μsec. If the oscillograph had its time-base circuit adapted to such short time variations, very complicated oscillograms were obtained from which it was necessary to deduce the individual variations. An example of such complicated oscillograms is reproduced in figure 4. In order to obtain a more general analysis of the variations it was also necessary to operate with a much slower time base. Oscillograms of this kind were better adapted to an analysis of consecutive partial discharges. Such oscillograms are exemplified in figure 5.

§ 7. DISCUSSION OF THE RESULTS

As has already been mentioned, our first measurements of the variation in the magnetic field were carried out without an amplifier. The advantage of this direct method was that it records where very rapid variations could be obtained without any distortion; its disadvantage was the limitation of sensitivity, and consequent restriction of the observational data which it involved.

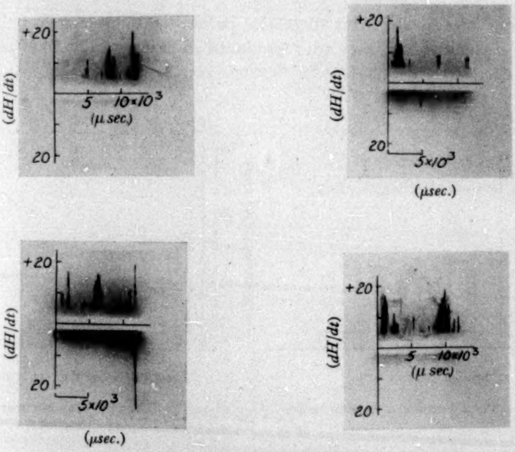


Figure 5. Oscillogram taken with frame aerial, with slow base time.

The advantage of the method now described was that it yielded a substantial increase in the number of observations within a relatively short observation period. On the other hand the improved method was not without inconveniences. With the increase of the distance between the place of observation and the lightning path a transformation in the form of the impulses must ensue. This was especially the case for the variation in the electric field. The influence was not so pronounced for the corresponding variation in the magnetic field and could be completely neglected in the case of the values given in this paper.

The distances between the lightning paths and the point of observation were sometimes so great in the present experiments as to render it possible that a damping effect might be influencing the results. The result of this damping must in the first place have been a slight alteration of the steepness of the front of the impulse in such a way that the time necessary for the current to reach its peak value became longer. A slight indication of such damping effects is visible in some of our records with the longest distances to the lightning path.

§ 8. THE CHARACTERISTIC PROPERTIES OF INDIVIDUAL CURRENT PULSES

The oscillograms provided data for a calculation of the total duration of the current pulses in fifty lightning discharges. The result is reproduced in figure 6, from which it is seen that the majority of the discharges had a duration below 0·005 sec.

The time intervals between successive partial lightning-current pulses for a number of 344 individual cases are reproduced in figure 7. The most usual time interval is characterized by values below 0·001 sec.

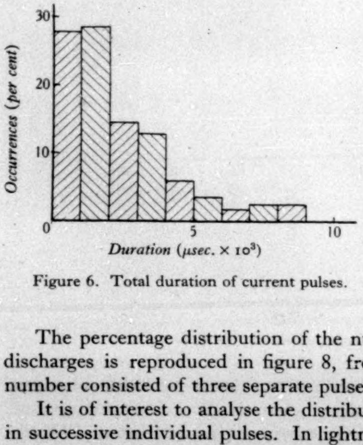


Figure 6. Total duration of current pulses.

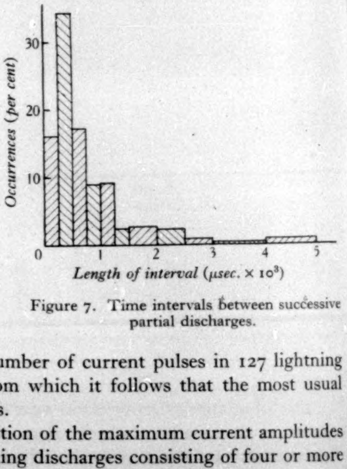


Figure 7. Time intervals between successive partial discharges.

The percentage distribution of the number of current pulses in 127 lightning discharges is reproduced in figure 8, from which it follows that the most usual number consisted of three separate pulses.

It is of interest to analyse the distribution of the maximum current amplitudes in successive individual pulses. In lightning discharges consisting of four or more current pulses the maximum current amplitudes were found in 85 per cent of the cases to occur in the two first pulses, or within the first half of the discharge. In the case of lightning discharges consisting of three pulses the maximum current was found quite as often in the first as in the second of the three discharges.

The percentage distribution of the total duration of individual pulses is reproduced in figure 9. The most usual values reached durations of from 20 to 60 μsec. In our first investigation the corresponding values were from 10 to 30 μsec. This difference in values can be fully explained by the difference in sensitivity during the two periods of observation. In our latest experiments we have used an especially sensitive method, by which impulses with low amplitudes and longer durations also could be recorded.

In 364 discharges we have calculated the time for the current to reach its crest value, and the results are reproduced in figure 10. The most usual values were from 6 to 8 or from 4 to 6 μsec., while earlier observations resulted in corresponding values of from 3 to 6 μsec.

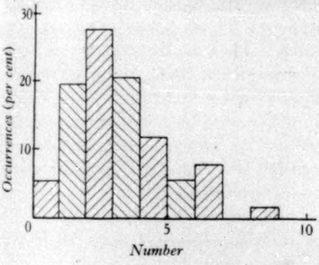


Figure 8. Number of partial discharges.

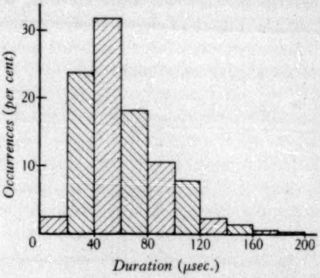


Figure 9. Total duration of individual pulses.

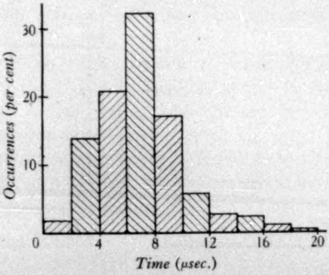


Figure 10. Time intervals for peak values of lightning current.

§ 9. CALCULATED HORIZONTAL COMPONENTS OF THE MAGNETIC FIELD

The horizontal components of the magnetic field in c.g.s. units have been calculated from observed vertical lightning discharges and are reproduced in figure 11. The positive sign is used to indicate that a positive charge goes to earth. Of eighty-eight recorded vertical lightning discharges 47 per cent were positive and 53 per cent negative, in full accordance with earlier results.

§ 10. CALCULATION OF THE MAXIMUM CURRENT-VALUES

During the observation period, vertical lightning discharges were in twenty-eight cases so located with regard to the observation station that it was possible to use the relation (3) for calculating the maximum current-values. The observations allowed of calculation for sixty-five partial discharges within the observed lightning paths, and the distribution of the values is shown in figure 12. The data are in full agreement with our earlier results, where the maximum amplitude reached was 120 kA. Figure 12 shows a considerable number of values as low as 1–5 or 6–10 kA. This occurrence of small currents is explained by the improvement in the sensitivity of the experimental methods.

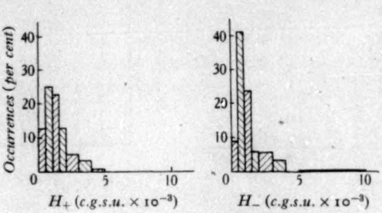


Figure 11. Horizontal components of magnetic field.

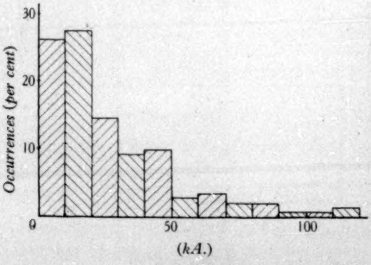


Figure 12. Distribution of peak values of individual current pulses.

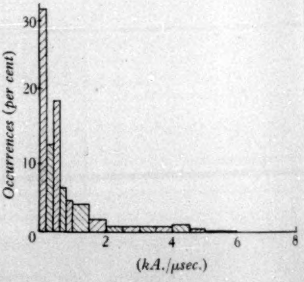


Figure 13. Maximal changes with time in lightning currents.

It is of special interest to compare the calculated maximum current-values with results from an independent and indirect method. On a large number of steel towers supporting high-tension power lines in the United States$^{(5)}$ and Germany$^{(6)}$, small steel links have been used to observe the maximum currents of lightning discharges which strike the towers. The steel of the link consists of a cobalt-nickel-iron alloy or a coal steel with high magnetic retentivity. A lightning stroke to a tower fitted with such a link resulted in magnetization of the link by the current.

The values of the magnetization could be determined subsequently, and from a knowledge of the magnetic constants and the location of the link on the tower it was possible to calculate the current passing through the tower. About 4000 observation stations were used in the United States for this purpose during the years 1932 to 1936.

The maximum observed value was 220·000 A. and there were relatively few values exceeding 100·000 A. The majority of the currents did not attain such high maximum values as 100·000 A. and were in very good agreement with our own values as regards their general distribution. The observational data from Germany were not so extensive as the data from the United States, but they also were in good agreement with our own results. An evident difference existed between our observations and those mentioned above. Both the American and the German observations resulted in a marked preponderance of negative currents, while our measurements indicated only a slight preponderance of this polarity. This smaller preponderance of negative values was quite in agreement with other and earlier observations of the polarity of the rapid variation in the electric field. It must be pointed out that the measurements made by the link method were carried out on very well earthed steel towers. Our measurements on the other hand were carried out in the open field. The marked preponderance of negative current-values for such structures as steel towers must, as we have found, be caused to a considerable extent by a polarity effect. Thus under the same conditions of field-intensity and charge-distribution, lightning discharges over steel structures will be much more easily developed at lower voltages when the cloud-polarity is negative than when it is positive.

From our observations it was possible to calculate the maximum changes of current with time in the lightning currents shown in figure 12. The result is graphed in figure 13. In our earlier investigations we obtained a few values of maximum current-changes amounting to 24–30 kA./μsec. These values were considered to be exceptional and have not recurred in the more recent work. Figure 13 shows also a preponderance of small changes of current with time, and this is to be expected with the improved sensitivity of our experimental methods.

REFERENCES

(1) Norinder, Harald. *J. Franklin Inst.* **218**, No. 6 (December 1934).
(2) Norinder, Harald. *Proc. Inst. Radio Engrs*, N.Y., **24**, No. 2 (February 1936).
(3) Norinder, Harald. *J. Franklin Inst.* **220**, No. 1 (July 1935).
(4) Norinder, Harald. *Z. Phys.* **63**, Heft 9 und 10 (1930).
(5) Lewis, W. W. and Foust, C. M. *Elect. Engng*, N.Y., **54**, No. 9, pp. 934–42 (September 1935).
(6) Zaduk, H. *Elektrotech. Z.* **56**, No. 17, pp. 475–9 (21 April 1935).

THE KNIFE-EDGE TEST FOR SPHERICAL ABERRATION

By R. KINGSLAKE, A.R.C.S., M.Sc., Institute of Applied Optics,
University of Rochester, U.S.A.

Received 17 *December* 1936. *Read* 28 *May* 1937

ABSTRACT. A method is given for computing the appearance seen in the knife-edge test, for various positions of the edge in various focal planes, when any specified amount of aberration is present. Series of patterns are given corresponding to (*a*) pure primary spherical aberration, and (*b*) zonal aberration with marginal correction.

§1. INTRODUCTION

THE knife-edge test as originally described by Foucault(1) was used as a means of ascertaining whether or not a telescope objective was perfect, and also as a guide in the improvement of an objective by local retouching. However, the knife-edge method may also be very usefully applied to lenses having considerable amounts of aberration, as has been shown by Miss Conrady(2).

It was felt desirable to extend this work, particularly in respect of spherical aberration. It will be realized that there is really a double infinitude of possible knife-edge shadows for a given lens, since the knife blade may be situated in any focal plane, and the edge itself may be advanced to any distance into the beam in that plane. In Miss Conrady's paper, only one shadow appearance is given for spherical aberration, namely that for the mid-position of the knife edge in a focal plane about midway between the marginal and paraxial foci.

The aim of the present paper is to explain a method by which the form of the shadow edge for any mixture of aberrations, at any specified position of the knife edge, may be computed.

§2. THEORY OF THE METHOD

It will be clear from elementary considerations that, if a lens possesses a considerable amount of spherical aberration, any zone of the lens will suddenly go dark as the knife edge cuts into its exact focus. Other zones of the lens, of which the foci lie beyond the knife plane, will darken on the side on which the knife is entering, whereas zones whose foci lie closer to the lens than this plane will darken on the opposite side. The result will be an appearance shown diagrammatically in figure 1.

The accurate computation of this and other shadow appearances can be made by differentiating the ordinary expression for spherical aberration as a path difference, namely:

$$P=\frac{A}{2l}r^2+\frac{B}{4l}r^4+\frac{C}{6l}r^6+\dots \qquad \dots\dots(1).$$

Here A represents a change of focus from the paraxial focal plane; B, C, etc. represent successive orders of spherical aberration; r is the radius of the zone; and l represents the distance of the image from the lens.

If we let (x, y) represent the two principal meridians of the lens, respectively perpendicular and parallel to the knife edge, then the path-difference may be written:

$$P=\frac{A}{2l}(x^2+y^2)+\frac{B}{4l}(x^2+y^2)^2+\frac{C}{6l}(x^2+y^2)^3+\dots \qquad \dots\dots(2).$$

By differentiating this, the components of the slope α of the ray from the point (x, y), relative to the ideal path of that ray, are obtained:

$$\left.\begin{aligned}\alpha_x&=\frac{A}{l}x+\frac{B}{l}x(x^2+y^2)+\frac{C}{l}x(x^2+y^2)^2+\dots\\ \alpha_y&=\frac{A}{l}y+\frac{B}{l}y(x^2+y^2)+\frac{C}{l}y(x^2+y^2)^2+\dots\end{aligned}\right\} \qquad \dots\dots(3).$$

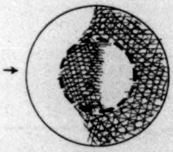


Figure 1. Knife-edge shadow, when knife blade is at focus of dotted zone (schematic).

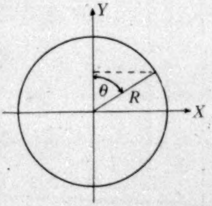


Figure 2. The principal meridians on the lens aperture.

These may be simplified by using polar coordinates on the lens aperture, figure 2, thus

$$\left.\begin{aligned}x&=r\sin\theta\\ y&=r\cos\theta\end{aligned}\right\} \qquad \dots\dots(4).$$

We now convert equation (3) to give the linear-displacement components ξ, η of the point at which the ray intersects the chosen focal plane. Since $\xi=-l\alpha_x$, $\eta=-l\alpha_y$, we have:

$$\left.\begin{aligned}\xi&=-\sin\theta\,[Ar+Br^3+Cr^5+\dots]=-K\sin\theta\\ \eta&=-\cos\theta\,[Ar+Br^3+Cr^5+\dots]=-K\cos\theta\end{aligned}\right\} \qquad \dots\dots(5).$$

The procedure for computing the knife-edge patterns is to calculate the values of K for a series of values of r, say $r=0{\cdot}1$, $0{\cdot}2$, $0{\cdot}3\dots1{\cdot}0$, and then tabulate the corresponding values of $\sin\theta$, equal to $-\xi/K$, for each of a series of values of ξ. The values of θ itself are then tabulated for all values of $\sin\theta$ less than unity. Now since each value of ξ represents a definite stage in the progress of the knife edge across the beam, the polar graph of (r, θ) for each value of ξ gives the appearance of the shadow edge for that position of the knife blade.

§3. THE PATTERNS FOR PRIMARY SPHERICAL ABERRATION

As an example, suppose it is desired to compute the shadows for pure primary spherical aberration, the knife blade being supposed to lie in the marginal focal plane. Then if $B=1$ (say), A will be -1, if r is taken as unity at the margin of the lens. Thus $K=r^3-r$ in this case. The values, with reversed sign, of sin θ and θ to the nearest degree, corresponding to a series of values of ξ, are shown in table 1.

Table 1

Values of $-\sin\theta$ and $-\theta$ (degrees) corresponding to given values of r and ξ. The values of θ are printe below those of sin θ.

r	·05	·1	·15	·2	·3	·4	·5	·6	·7	·8	·9
$-K$ $-\xi$	·050	·099	·147	·192	·273	·336	·375	·384	·357	·288	·171
·05	1·002 —	·505 30°	·344 20	·265 15	·183 11	·149 9	·133 8	·130 7	·140 8	·173 10	·292 17
·10	2·0 —	1·01 —	·688 43	·521 32	·366 21	·298 17	·267 15	·260 15	·280 16	·347 20	·585 36
·15	— —	— —	— —	·786 52	·549 33	·447 26	·400 24	·390 23	·420 25	·520 32	·877 61
·20	— —	— —	— —	— —	·732 47	·596 36	·534 32	·520 31	·560 34	·694 44	— —
·30	— —	— —	— —	— —	— —	·894 63	·801 54	·780 53	·840 58	— —	— —
·40	—	—	—	—	—	—	—	—	—	—	—

These values are most conveniently plotted on ordinary polar-curve paper, a circle of ten units diameter being taken to represent the rim of the lens aperture. Graph points are marked on this corresponding to all the available pairs of values of r and θ, figure 3. The locus of all points having the same value of ξ represents the

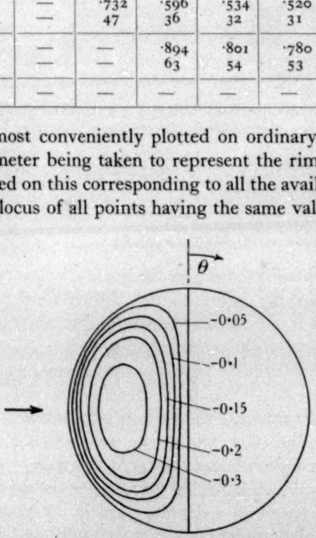


Figure 3. Computed shadow edges for primary spherical aberration, in marginal focal plane.

edge of the shadow corresponding to a knife-position given by ξ; thus by this method the whole family of shadow-boundaries are plotted on the same figure. They can be then traced off in turn and collected as shown in figure 4. For the different focal planes in the diagram, the values of A were respectively $-1{\cdot}5$, $-1{\cdot}0$, $-0{\cdot}5$, 0, and $0{\cdot}5$.

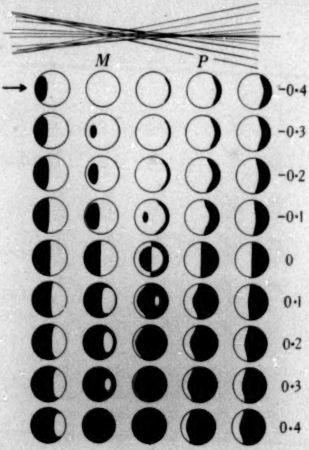


Figure 4. The knife-edge shadows for primary spherical aberration (computed).

In figure 5 is shown a series of actual photographs of knife-edge shadows made on a reversed telescope objective, the position of the knife blade being removed progressively further from the lens from left to right. The knife edge was advanced in each case from above to a point as near to the lens axis as could be secured.

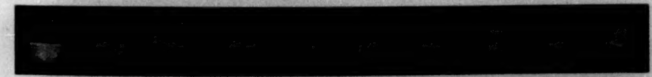


Figure 5. Knife-edge shadow photographs for a reversed telescope objective.

One very characteristic feature of this test is the appearance seen when the knife blade is at the paraxial focus. The central patch of shadow is seen to jump suddenly across the centre of the aperture for an infinitesimal advance of the knife blade. This appears to be the only method of experimentally locating a paraxial image point, since it does not require the stopping down of the lens to a small hole with the consequent great increase in the depth of focus.

§4. THE PATTERNS FOR ZONAL ABERRATION

In the case of zonal aberration, since the marginal aberration is to be zero, the values taken were $B = +1$, $C = -1$, A having the values $-0{\cdot}375$, $-0{\cdot}25$, $-0{\cdot}125$, 0, $+0{\cdot}125$ respectively, and ξ the values $-0{\cdot}15$, $-0{\cdot}10$, $-0{\cdot}05$, $-0{\cdot}01$, and 0.

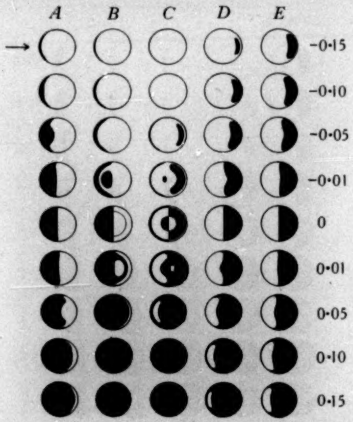


Figure 6. The computed knife-edge shadows for zonal aberration.

The plane for which $A = -0{\cdot}25$ (column B, figure 6) is the plane of the minimum zonal focus, namely the focus of the zone with r equal to $0{\cdot}707$. Column D corresponds to the united marginal and paraxial focus, in which plane the coefficient $A = 0$.

§5. CONCLUSION

In the discussion given above, only the first two orders of spherical aberration have been considered; the same method is of course applicable to the computation of knife-edge shadows for any single aberration or mixture of aberrations which is expressible as a path difference in equation 1. When aberrations such as coma or astigmatism, which do not have rotation symmetry about the lens axis, are present, it is clear that different shadow patterns will be obtained for different directions of entry of the knife blade. Some examples of these are given by Miss Conrady in the paper cited.

REFERENCES

(1) Foucault. *Mon. Not. R. astr. Soc.* **19**, 284 (1859).
(2) Conrady, H. G. *Trans. opt. Soc.*, Lond., **25**, 219 (1924).

THE VELOCITY-DISTRIBUTION IN A LIQUID-INTO-LIQUID JET

BY E. N. DA C. ANDRADE, F.R.S., Quain Professor of Physics
in the University of London

AND

L. C. TSIEN, B.Sc.

Received 5 *April* 1937. *Read* 7 *May* 1937

ABSTRACT. The distribution of velocity in a liquid-into-liquid jet, issuing from a cylindrical tube with a tapering approach, has been measured by photographing the traces made by suspended particles, with strong illumination and a determined exposure. The results have been compared with the theory for a jet issuing from a point in an infinite plane, and it is shown that, supposing the equivalent point source to be within the orifice, good agreement is found except in the immediate neighbourhood of the orifice. An expression has been derived connecting the distance of the equivalent point source from the orifice with the Reynolds's number. This enables the loss of kinetic energy of the jet to be worked out.

§ 1. INTRODUCTION

FOR some time experiments have been in progress in the physics laboratory at University College, London, on the instability of a liquid-into-liquid jet. In particular, attention has been devoted to the nature of the motion produced by a periodic disturbance, acting on a fine jet of water flowing through a circular orifice into a shallow tank of water. In this connexion it is of interest to determine the distribution of velocity in the undisturbed jet, especially as comparatively little has been done experimentally on streaming without rigid walls.

The behaviour of a laminar jet of viscous liquid has been recently worked out by Schlichting(1) on certain simplifying assumptions, of which the most serious is that the jet issues from a point aperture, giving, as it does, an infinite velocity. One of the objects of this work was, therefore, to see how far Schlichting's theory could be applied to an actual jet, issuing from a circular aperture of finite size. The theory has proved to be very successful in interpreting the results, and it is shown here how, with slight modification, it can be made to give the velocity everywhere except in the immediate neighbourhood of the orifice. One consequence of this work is that the loss of kinetic energy due to viscosity can be worked out.

§ 2. EXPERIMENTAL METHOD

The experiments, being carried out in a physical laboratory, had to be done on a small scale. The internal profile of the glass jet used is given in figure 2, which shows a photograph obtained by immersing the glass jet, full of air, in a liquid of the same refractive index as the glass, contained in a glass tank with plane sides. The diameter of the orifice was 0·91 mm. The water used contained very fine suspended particles. A horizontal plane through the axis of the jet was strongly illuminated, and photographed with a measured short exposure. The tracks of particles, both in the water constituting the original jet and in the surrounding liquid, appeared as short lines terminating sharply, the lengths giving a measure of the velocity at the mid-point of the line. From these tracks, then, the velocity distribution could be obtained. Subsidiary experiments gave the volume per second passing through the jet at various pressures, measured in the straight approach tube. The pressure in this tube was used to control and determine the mean velocity of efflux.

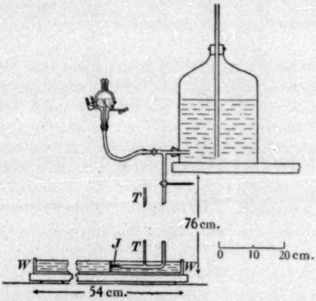


Figure 1.

The general arrangement of apparatus is shown in figure 1. Water from a large Mariotte's bottle, containing about 7 litres, was admitted, by a tap capable of accurate adjustment, to a vertical tube, leading to the jet *J*. The vertical tube *TT* allowed the pressure to be read by a cathetometer. The tank *WW* rested on a massive slate slab, supported on folded cloths, to minimize vibration. The level in the Mariotte's bottle was measured on a Casella sensitive pressure gauge, based on the internal reflection of a pointer from the surface of the water, reading to 0·01 mm. This was used to calibrate the outflow against the pressure, the time for the level to fall through 2 mm. being taken on a stop watch, and the corresponding volume being determined independently. The temperature was always maintained at 18° C., so that changes of viscosity had not to be considered.

Various particles were tried, including fish scales (as used for the manufacture of artificial pearls), flue dust and a powdered magnesium-aluminium alloy. Aluminium particles from commercial aluminium powder were finally adopted. The

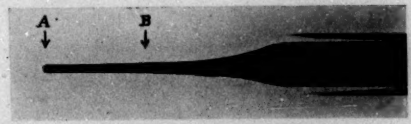


Figure 2. (Magnification × 1·5.)

Figure 3*a*. (Magnification × 9·4.)

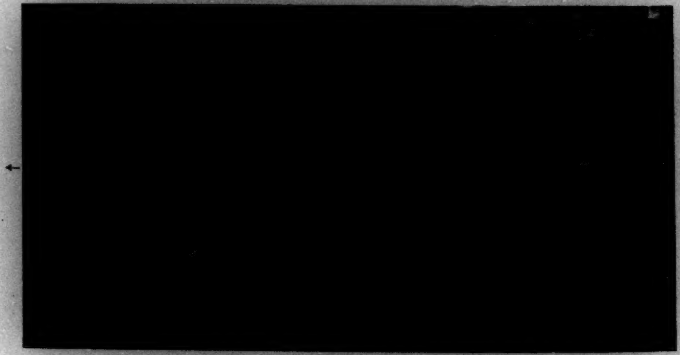


Figure 3*b*. (Magnification × 9·2.)

To face page 383

powder was washed in a separating funnel with alcohol, to remove grease, and the coarser particles run off. The alcohol was then filtered off from the remaining particles, which were dried and then suspended in distilled water, in a vessel about 5 ft. high. The suspension was allowed to stand for about 15 min., and the middle part of the liquid column then drawn off. This liquid, diluted with a large bulk of water, was used for the experiments, being placed both in the tank and in the supply bottle. The particles were from 0·05 to 0·08 mm. in diameter.

For illumination, a 55 A. arc was focused on to a horizontal slit by a wide-angle condensing lens, and an image of the slit formed on the axis of the jet stream by a 1½ in. Mayer lens of aperture $f/1\cdot 5$. This image was about 0·1 mm. wide, so that, even allowing for the convergence and divergence of the beam away from the axis, only a central section of the jet was illuminated. To photograph the tracks a similar lens, by Dallmeyer, was used, which gave a magnification of 5 with the distances adopted. The plates were Ilford hypersensitive panchromatic, speed 8000 H. and D. to ½-watt illumination.

A shutter was required which would give exposures of some thousandths of a second with an accuracy of 1 per cent or better. This was provided by a rectangular aperture in a weighted board, falling freely in its own plane under gravity; the horizontal edges of the aperture were accurately straight, and their separation was 2·3 cm. in the normal case, giving an exposure of 0·00782 sec. Another aperture often used gave an exposure of 0·00497 sec. The shutter fell within 2 mm. of the illuminating slit, and was controlled by a magnetic release.

The plates obtained gave sharply terminated lines, as exemplified in figures 3 *a* and 3 *b*, which are selected as showing typical results at two different velocities. To measure up a plate a reference line, drawn parallel to the axis of flow, was taken as a provisional x axis, the y axis being the normal to the axis through the orifice. The length of track was recorded against the coordinates of the mid-point of the track, several photographs being taken for each rate of efflux, so as to provide sufficient material. The exact position of the x axis was then obtained from considerations of symmetry. A standard value of x being selected, the velocity at this distance was obtained, if necessary by interpolation, for different values of y. Three different values of x were used, viz. 0·8, 1·8 and 3·3 cm.

§ 3. TREATMENT OF RESULTS

Schlichting's treatment, which is based on the neglect of the radial accelerations, in the sense of the boundary layer theory, leads to expressions for u and v, the longitudinal and radial velocities, of the following form:

$$u=\frac{3}{8\pi}\frac{K}{\nu x}\frac{1}{(1+\xi^2/4)^2},\qquad v=\frac{1}{4}\sqrt{\frac{3K}{\pi}}\cdot\frac{1}{x}\cdot\frac{\xi-\xi^3/4}{(1+\xi^2/4)^2}\qquad\text{......(1)},$$

where

$$\xi=\sqrt{\frac{3K}{16\pi}}\cdot\frac{1}{\nu}\cdot\frac{y}{x}\quad\text{and}\quad K=\frac{J}{\rho},$$

J being the momentum crossing a plane normal to the axis of the jet per second, ν the kinematic viscosity and ρ the density of the fluid. The distance x is measured parallel to the axis, from the point origin of the jet. The jet draws the surrounding liquid along, the theoretical stream lines in a particular case being given in figure 9.

We can express u in the following form:

$$u = A\frac{1}{(1+By^2)^2} \qquad \text{......(2)},$$

where

$$A = \frac{3K}{8\pi\nu}\frac{1}{x}, \quad B = \frac{3K}{64\pi\nu^2}\frac{1}{x^2},$$

so that

$$A/B = 8\nu x.$$

If then we plot the experimental values of $1/\sqrt{u}$ against y^2 we should obtain a straight line, and this expectation has been realized. The intercept on the vertical axis gives $1/\sqrt{A}$, and the slope of the line gives $B/\sqrt{A}$, from which A and B can be calculated. With the values of A and B so found theoretical curves of u against y have been drawn for comparison with the experimental points.

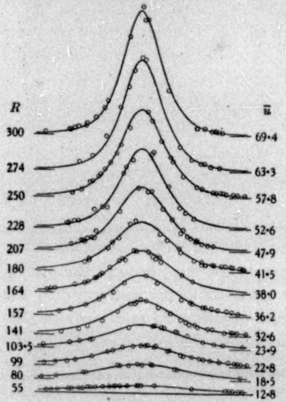


Figure 4.

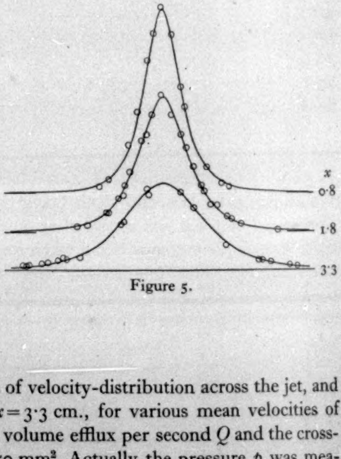


Figure 5.

Figure 4 shows the theoretical curves of velocity-distribution across the jet, and the experimental points, at a distance $x = 3{\cdot}3$ cm., for various mean velocities of flow in the jet itself, calculated from the volume efflux per second Q and the cross-sectional area of the jet, which was 0·650 mm.^{2} Actually the pressure p was measured in each experiment, and Q found from the experimental curve connecting Q and p. It will be seen that over a wide range (Reynolds's number in the tube, taken as $R = \bar{u}a/\nu$, where a is the radius of the orifice, varies from 55 to 300) the agreement between the theoretical and experimental forms is excellent. The results at three different distances from the jet, viz. $x = 0{\cdot}8$, $1{\cdot}8$, $3{\cdot}3$ cm., with a fixed value of $\bar{u} = 46{\cdot}7$ cm./sec., are shown in figure 5, where the agreement is equally satisfactory.

§4. THE MOMENTUM OF THE JET

Velocity-distributions were measured at each of the known distances just specified, with various values of $\bar{u}$, and in this way a series of values of A and B were obtained. Now according to theory,

$$A/B = 8\nu x \qquad \text{......(3),}$$

and

$$K = \frac{\pi}{3}\frac{A^2}{B} = 1{\cdot}047\frac{A^2}{B} = \frac{J}{\rho} \qquad \text{......(4),}$$

$$= J \text{ in the case of water.}$$

Equation (4) enables us to find a value for J from each velocity profile measured. These various values are shown in figure 6, plotted against the pressure in centimetres of water, and it will be seen that the measurements made at three different distances are consistent.

The volume issuing from the jet per second has been measured in terms of the pressure, but to find the momentum we must know the velocity-distribution at the orifice, for which we have to consider whether, with the short tube used, the influence of the entry extended to the orifice. At first sight it would seem that we have as a guide the work of Schiller[(2)], who finds that the Poiseuille regime sets in at a distance l from the entry given by

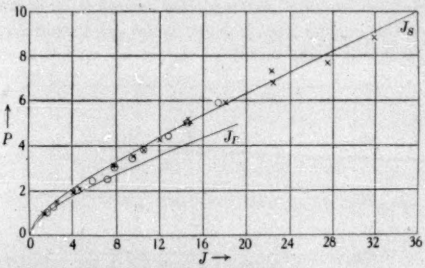


Figure 6. ×, $x=3{\cdot}3$ cm.; ○, $x=1{\cdot}8$ cm.; +, $x=0{\cdot}8$ cm.

$$l/d = 0{\cdot}029\,R.$$

Taking for l, the effective length of our tube, 1·2 cm., which corresponds to the length AB in figure 2, and a mean diameter of 0·103 cm., we find that R must not exceed 400, which would indicate that the parabolic distribution is only beginning to fail at our highest speeds. However, it has been shown that even a slight convergence in a tube (1 mm. in radius on a length of 1 m., while $R=1000$) causes a marked flattening in the velocity-distribution[(3)],* while, for the case of convergent parallel walls (two-dimensional streaming) Hamel[(4, 5)] has shown that U deviates markedly from $U_{\max}$ only at the walls, the velocity being uniform across almost the whole cross-section. We may anticipate, then, that with our convergent nozzle the velocity-distribution across the orifice will be practically square-headed. This anticipation is confirmed when we come to compare the momentum, as deduced from velocity-profile measurements in the jet (where $J = 1{\cdot}047\ A^2/B$) with that calculated from the volume efflux Q per second at the corresponding pressure-head. To find J from Q we must know the velocity-distribution at the orifice; for a parabolic distribution the momentum $J_P = \frac{4}{3}\rho Q^2/\pi a^2$, while for a square-headed distribution the momentum $J_S = \rho Q^2/\pi a^2$. In figure 6 the two curves J_P and J_S, computed from the experimental curve of Q against p, are shown, and it will be seen that, except from the smallest values of R, the points deduced from the velocity-profile agree closely with J_S, indicating a uniform velocity across the jet. It would appear that the parabolic distribution with our particular jet ceases when $R =$ about 80 or less, and the uniform velocity-distribution is certainly in force when $R >$ about 180.

---

* Dr Tietjens informs me that the calculations, on which the figure given in his book[(3)] is based, were carried out by himself, but that details have never been published.

§ 5. EFFECTIVE ORIGIN OF THE JET

Referring to equation (3), we see that for a given value of x the ratio A/B should be independent of the momentum of the jet. Our experimental results show, however, that A/B increases as the momentum increases, as is shown in figure 7, where the dimensionless quantity $(\nu a)^{-1}\ A/B$ is plotted against R. It is clear that if the jet is to be considered as coming from a point, as the calculation assumes, then that point must be taken not at the mouth of the jet but within it, and the distance x_0 of this imagined point source from the orifice must increase as the momentum increases and the angle of the jet becomes smaller. The simplest assumption, which will be justified by considerations of the kinetic energy, is that x_0 is proportional to Q, or, what is the same thing, to $\bar{u}$, so that

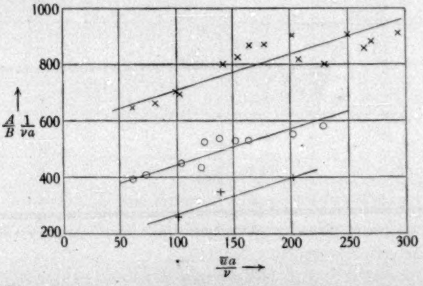


Figure 7. ×, $x = 3{\cdot}3$ cm.; ○, $x = 1{\cdot}8$ cm.; +, $x = 0{\cdot}8$ cm.

$$A/B = 8\nu\,(x + x_0)$$

or

$$\frac{1}{\nu a}\frac{A}{B} = \frac{8}{a}(x + x_0) = 8\left(\frac{x}{a} + \frac{x_0}{a}\right).$$

This enables us to find a value of x_0 corresponding to each value of A/B. In figure 8, x_0/a is plotted against $\bar{u}a/\nu$, and it will be seen that the values obtained at the three different values of x are quite consistent. The points show a certain scatter, but it is clear that the method of fixing x_0 makes severe demands on the data, and that discrepancies of a millimetre or two, that is, of 10 to 20 per cent, are to be anticipated. The results can be roughly represented by a straight-line relationship, shown by the full line in the figure, which gives

$$\frac{x_0}{a} = 0{\cdot}160\,\frac{\bar{u}a}{\nu} = 0{\cdot}160R \qquad \ldots\ldots(5)$$

or

$$\frac{1}{\nu a}\,\frac{A}{B} = 8\left(\frac{x}{a} + 0{\cdot}160\,\frac{\bar{u}a}{\nu}\right).$$

The three straight lines in figure 7 correspond to this formula, and it will be seen that they represent the experimental results as well as can be expected. In particular one value of x_0, corresponding to a given value of $\bar{u}a/\nu$, represents the results at all three values of x: the separation of the three straight lines, which all have the same slope, is not arbitrary, but given by the formula.

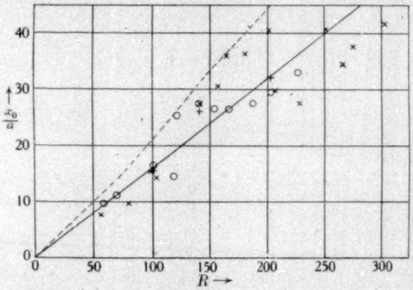


Figure 8. ×, $x = 3{\cdot}3$ cm.; ○, $x = 1{\cdot}8$ cm.; +, $x = 0{\cdot}8$ cm.

In view of the conditions at the orifice, it might at first sight be supposed that the distance of the effective point source within the tube would be such as to make the theoretical lines of flow at the boundary of the orifice continuous with the walls of the tube; that is, that at this boundary $v = 0$ and $\partial v/\partial x = 0$ for the flow from the point. On reference to the expression for v in equation (1), it is seen that $v = 0$ if $\xi = 2$, which also gives $\partial v/\partial x = 0$. From the expression for ξ we find, remembering that $\rho = 1$ and

$$J_S = \frac{\rho Q^2}{\pi a^2} = \pi \nu^2 R^2,$$

$$\frac{\sqrt{3}}{4}\,R\,\frac{y}{x} = 2 = \frac{\sqrt{3}}{4}\,R\,\frac{a}{x_0} \text{ at the orifice}$$

or

$$\frac{x_0}{a} = \frac{\sqrt{3}}{8}\,R = 0{\cdot}216\,R.$$

This neglects, however, the fact that the tube and its baffle will interrupt the theoretical lines of flow due to the point source, so that the constant multiple of R cannot be expected to have the value 0·216. It is of interest to note, however, that these considerations give a formula of the same type as equation (5).

To illustrate this point figure 9 has been prepared. It shows the lines of flow from the point P, taken at a distance x_0 within the jet given by equation (5), the value of R being 200. The lines are shown broken where they lie within the jet and baffle. It is clear that in the liquid half space they cannot have exactly the form shown near the baffle, but it is also clear that only a slight modification is required to make them conform to the actual boundary conditions. The continuity of the tube of flow FF with the walls of the jet appears to the eye to be quite good, but actually the point at which $v=0$ is some little distance outside the jet, and is marked with an arrow. The diagram makes it easy to see how it is that the flow from a point source suitably chosen gives a good representation of the actual flow, except in the immediate neighbourhood of the jet. For completeness the velocity-profiles at the three distances A, B and C are given. The scale of x is ten times that of y.

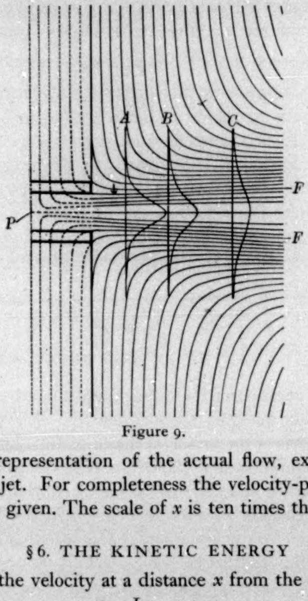


Figure 9.

§ 6. THE KINETIC ENERGY

If we assume that the velocity at a distance x from the orifice is given by

$$u=\frac{3}{8\pi}\cdot\frac{J}{\eta x'}\cdot\frac{1}{\left(1+C\,\frac{y^2}{x'^2}\right)^2},$$

where

$$C=\frac{3}{64\pi}\cdot\frac{J}{\rho\nu^2}\quad\text{and}\quad x'=x+x_0,$$

we can derive an expression for the kinetic energy in terms of x_0. Schlichting's calculation with a point source gives, of course, an infinite velocity and energy at the orifice.

The kinetic energy E passing per second through a plane distant x from the end of the tube is given by

$$\begin{aligned} E &= \pi\rho \int_0^\infty u^3 y\, dy \\ &= \frac{27\rho}{512\pi^2}\,\frac{J^3}{\eta^3 x'^3}\,\frac{x'^2}{10C} \\ &= \frac{9}{80\pi}\,\frac{J^2}{\nu\rho x'} = \frac{9}{80\pi}\,\frac{J^2}{\nu\rho\,(x+x_0)} \qquad \text{......(6),} \end{aligned}$$

or at the orifice

$$E_0 = \frac{9}{80\pi}\,\frac{J^2}{\nu\rho x_0} \qquad \text{......(7).}$$

A value for x_0 may be obtained by comparing this with the kinetic energy at the orifice as determined by the flow in the tube, which will, however, depend upon the velocity profile assumed. For the parabolic distribution at the orifice

$$J_p = \frac{4}{3}\,\frac{\rho Q^2}{\pi a^2}$$

and

$$E_0 = \frac{\rho Q^3}{\pi^2 a^4} = \frac{9}{16}\,\frac{J^2}{\rho Q},$$

while for the rectangular distribution

$$J_S = \frac{\rho Q^2}{\pi a^2} \text{ and } E_0' = \frac{1}{2}\,\frac{\rho Q^3}{\pi^2 a^4} = \frac{1}{2}\,\frac{J^2}{\rho Q}.$$

Comparing these values with equation (7) we have for the parabolic profile

$$x_0 = \frac{1}{5\pi\nu}\,Q \text{ or } \frac{x_0}{a} = 0{\cdot}200\,R \qquad \text{......(8),}$$

and for the rectangular profile

$$x_0 = \frac{9}{40\pi\nu}\,Q \text{ or } \frac{x_0}{a} = 0{\cdot}225\,R \qquad \text{......(9),}$$

so that the difference between the two cases is not large. As we have seen, when $R < 80$ the value of x_0 should be given by equation (8), while when $R > 180$, or earlier, it should be given by equation (9). The broken line, figure 8, represents the values of x_0 which comply with these conditions. At the higher values of R the values of x_0 derived from the momentum conditions are nearly 30 per cent smaller.

The reason for this discrepancy lies in the nature of the orifice conditions given by the assumption of a point origin within the tube. The actual velocity profile at the orifice varies from parabolic to square, according to R, while the assumption of a point source within the tube must give at the orifice a profile of the form shown in figures 4 and 5. Figure 10 shows, for a particular value of R, the profile from a point source compared with the parabolic and square profiles which give, about the x axis, the same second moment for the enclosed area, i.e. the same momentum at the orifice. The kinetic energy given by the actual profile must clearly, in this case, be less than that given by the assumption of a point source, or, in other words, we must on this assumption increase x_0 to get the right kinetic energy.

The difference between the value of x_0 given by the momentum distribution and by comparison of the kinetic energies at the orifice is, then, due to the fact that the latter method involves the distribution at the orifice itself. When the distance from the orifice exceeds a certain value (which is not greater than 0·8 cm. with our jet of diameter 0·09 cm.) the velocity-distribution, and therefore the kinetic energy, is given to a close approximation by substituting the value of x_0 given by equation (5) in

$$E=\frac{9}{80}\frac{\rho Q^4}{\pi^3 a^4 \nu}\frac{1}{x+x_0}$$

if the distribution at the orifice is rectangular ($R>180$ with our type of jet). The energy is only $\frac{9}{8}$ times greater if the distribution is parabolic.

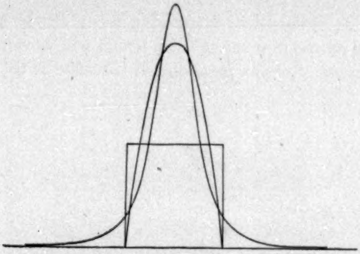


Figure 10.

As regards the loss of kinetic energy which takes place in the jet, for larger values of R we have then

$$\frac{E}{E_0}=\frac{x_0+x}{x_0}=1+\frac{x}{0{\cdot}225\,Ra}.$$

§7. ACKNOWLEDGEMENTS

We have had the advantage of discussing certain points with Professor L. N. G. Filon, F.R.S., to whom our best thanks are due. The lenses used in the photography were originally purchased from a grant generously made by the Imperial Chemical Industries, Ltd.

REFERENCES

(1) Schlichting. *Z. angew. Math. Mech.* **13**, 260 (1933).
(2) Schiller. *ForschArb. Ver. dtsch. Ing.* No. 248 (1922).
(3) Prandtl-Tietjens. *Applied Hydro- and Aeromechanics*, p. 54 (London, 1934).
(4) Hamel. *Jber. dtsch. MatVer.* p. 34 (1916).
(5) Tollmien. In *Handb. Exp. phys.* **4**, pt. 1, p. 257 (Leipzig, 1931).

DISCUSSION

Mr J. H. Awbery. I wonder whether Prof. Andrade would consider that the formula given for the effective position of the source can be applied generally, even with jets of somewhat different convergence, or whether the coefficient 0·16 is dependent on this factor.

Dr A. B. Wood. A point of great interest is centred at the orifice of the tube, and it would be valuable if the authors could extend their observations (if they have not already done so) to the liquid flow near this point, just inside and just outside the tube.

Dr J. E. R. Constable. With regard to the authors' deduction that, except for low rates of flow, there was an approximately uniform velocity-distribution in the water flowing in the tubes they tested, I should like to ask whether they expect a similar distribution in the gas emerging from a sensitive-flame jet. I understand that the work described in this paper had its inception in a study of the action of sensitive flames.

Miss T. J. Dillon. Could this method be applied to experiments on a blast of air from a jet if suitably light particles were used?

S. R. Bennett. I should like to ask the authors whether the method could be applied to distinguish between the particles originating in the jet itself and those entrained from the surrounding fluid.

Authors' reply. In reply to Mr Awbery and Dr Constable: As long as the velocity is uniform across the orifice the coefficient 0·160 will be appropriate. As is pointed out in the paper, this uniformity of velocity is to be expected so long as the Reynolds's number $\bar{u}a/\nu$ is not very small and so long as the jet does not terminate in a very long uniform tube—that is, so long as it is of anything like the form used in our experiments. In reply to Dr Wood: We tried to measure the velocity in the immediate neighbourhood of the orifice as has been suggested by Dr Wood, but were not successful. We are not clear as to the reason for the unsatisfactory nature of our plates for this region. In reply to Miss Dillon: The method could undoubtedly be applied to a non-turbulent air blast. In reply to Mr Bennett: In order to differentiate between the particles originating in the jet and those entrained, some colouring matter should be introduced into the liquid which issues from the jet. This then distinguishes it from the liquid through which it flows, but does not obscure the particles if a suitable concentration is chosen. We have actually done this in certain experiments.

SECONDARY-ELECTRON EMISSION FROM COMPLEX SURFACES

By L. R. G. TRELOAR, B.Sc., F.Inst.P.

(Communication from the Research Staff of the M.O. Valve Company, Limited, at the G.E.C. Research Laboratories, Wembley, England.)

Received 19 *February* 1937. *Read* 7 *May* 1937

ABSTRACT. The secondary emission from metals on whose surfaces foreign substances (e.g. electropositive metals) have been deposited to various thicknesses up to a few atomic layers has been studied. It is shown experimentally that for sufficiently thin films of the contaminant the secondary emission for a given base metal depends only on the work function of the surface, and not at all on the nature of the contaminant. The form and magnitude of the variation of secondary emission with work function agree with those calculated from the energy-distribution of secondary electrons. From a study of thicker films information is obtained concerning the mean depth of liberation of secondary electrons. The significance of the results in connexion with more complex secondary-emitting materials is discussed.

---

§ 1. INTRODUCTION

The possibility of making use of secondary-electron emission to obtain an amplification of electronic currents has led to a search for materials having high secondary-emission coefficients. Thus it has been found that certain metallic oxides, after treatment with alkali metal vapours, yield secondary-emission coefficients very much higher than any that have been obtained from clean metals. One of the best of these emitters is caesium on caesium oxide on silver, formed by heating oxidized silver at 200° C. in caesium vapour. This material, which is frequently employed as a photoelectric cathode, has been found by Penning and Kruithof(1) to give a secondary-emission coefficient of between 8 and 10 at 500 volts, and similar values have been reported by other workers.

It is clear that the materials which give these high secondary-emission values have also very low work functions. It is probable, therefore, that the work function must be regarded as one of the fundamental physical factors by which the magnitude of the secondary-emission coefficient is determined. But it is not necessarily the only factor. It is the purpose of the present investigation to determine to what extent changes of work function, unaccompanied (so far as this is possible) by other changes, affect the secondary-emission coefficient.

§ 2. METHOD OF TREATMENT

The work function of a material may be changed by depositing on its surface a thin film of a different material. Thus, for example, the work function of tungsten may be reduced by several electron-volts by the adsorption on its surface of a barium layer less than one atom thick, and the thermionic emission is increased by a large factor as a result of the reduction in the energy which an electron is required to possess in order to pass through the surface.

When a metal is bombarded with electrons the secondary electrons, which originate beneath the surface⁽²⁾, must lose energy in passing through the surface, in exactly the same way as the thermally emitted electrons. It is to be expected that, in general, there will be some secondary electrons approaching the surface from within which have insufficient energy to escape; these electrons will fall back into the interior of the metal. The relative number of such electrons will clearly depend on the work function, becoming smaller as the work function is reduced. We should therefore expect the relative number escaping, i.e. the secondary-emission coefficient, to increase if the work function of the metal is reduced, for example, by the presence of an adsorbed layer of foreign atoms.

Furthermore, given a knowledge of the energy-distribution of the secondary electrons, it should be possible to calculate how the relative number of electrons escaping will be affected by a given change in the work function.

This calculation is made in the following pages, and the resulting relationship between secondary emission and work function is compared with that found experimentally for a metal contaminated with different substances.

§ 3. THEORETICAL EXAMINATION OF THE RELATION BETWEEN SECONDARY EMISSION AND WORK FUNCTION

The general case. The argument outlined in the preceding paragraph, which will now be developed quantitatively, depends for its validity upon the assumption that the adsorbed film itself neither absorbs primary electrons nor emits secondary electrons. Any effect which it has on the secondary-emission coefficient will be considered to take place solely through the agency of the accompanying changes in work function.

The energy corresponding to the component of velocity normal to the surface will be referred to as the *normal energy* of the secondary electrons. In considering the effect of the work function on the energy of the escaping secondary electrons it is the normal energy only which will be modified, since there are no electrical forces parallel to the surface.

The normal energy distribution of the secondary electrons escaping from a clean metal may be written in the form

$$dn = f(u)\,du \qquad \text{......(1)},$$

where dn is the number of electrons having normal energy between u and $u+du$, measured in electron-volts.

The total number having normal energy greater than any positive value U will be

$$n = \int_U^\infty f(u)\,du \qquad \text{......(2)}.$$

If the work function of the metal is now increased by an amount χ eV. by a suitable contamination, only those electrons which formerly escaped from the clean metal with normal energy greater than χ will now be able to escape, and the number n of such electrons will be given by

$$n=\int_{\chi}^{\infty} f(u)\, du \qquad \text{......(3).}$$

If δ_0 and δ are the secondary-emission coefficients for the clean and contaminated metal respectively, it follows that

$$\frac{\delta}{\delta_0}=\frac{\int_{\chi}^{\infty} f(u)\, du}{\int_{0}^{\infty} f(u)\, du} \qquad \text{......(4).}$$

It is therefore possible by means of equation (4) to calculate the effect of an increase of work function on the secondary-emission coefficient, provided that the normal energy distribution of the secondary electrons from the clean metal is known.

The effect of a reduction of work function, with which this paper is mainly concerned, cannot be calculated with the same accuracy, since it is necessary to extrapolate the distribution function represented by equation (1) into the region of smaller values of energy, for which u is negative. (The quantity u in equation (1) represents the energy of the electrons outside the metal. An electron whose energy within the metal is less than the minimum energy which it must possess in order to escape by an amount u may therefore be said to possess an energy $-u$.) If such an extrapolation can be made, the secondary-emission coefficient of the contaminated surface may likewise be deduced from equation (4), but in this case the change of work function χ will be negative.

Application to Maxwellian distribution. If the secondary electrons have an energy-distribution represented by Maxwell's Law, equation (1) becomes

$$du=Ae^{-\alpha u}\, du \qquad \text{......(5),}$$

where A and α are constants. Substitution in (4) gives

$$\frac{\delta}{\delta_0}=\frac{A}{\alpha}\, e^{-\alpha\chi}$$

or

$$\log_{10}\delta=C-b\chi \qquad \text{......(6),}$$

where C and b are constants, δ_0 being fixed. If in this equation χ is taken as the independent variable, it is seen that for a given metal, variously contaminated, the logarithm of the secondary-emission coefficient varies linearly with the work function.

An equation equivalent to equation (6) has been derived theoretically by Sixtus(3) for the special case of a Maxwellian distribution of energy. Sixtus also measured the secondary-emission coefficient and work function for a thoriated tungsten filament in different states of activation. He found the equation to be applicable over a limited range of work functions, but the coefficient b was found to vary greatly with the energy of the primary electrons. These results will be considered in greater detail later.

Derivation of normal energy-distribution. Before considering the applicability of the results deduced in the preceding sections, it is necessary to examine the available data on the energy-distribution of secondary electrons. The first point to be noted is that there are no experimental data for the *normal* energy-distribution. Such measurements as have been made on the energy-distribution fall into the following two classes.

(*a*) The retarding potential method. In this method the secondary electrons from a target are collected by a chamber (usually spherical) surrounding it, to which negative potentials with respect to the target are applied. Provided that the chamber is large compared with the target, this method gives the integral of the *total* energy-distribution curve, i.e. the number of electrons having total energy greater than any given value.

(*b*) The magnetic-spectrum method. In this method a beam of secondary electrons from a target is deviated by a magnetic field, and the total energy-distribution is obtained directly.

The most accurate work on the total energy-distribution is probably that of Haworth, who has obtained curves for molybdenum(4) and columbium(5) by method (*b*). His data for molybdenum will be taken as a basis for the calculations which follow. Curve *a* in figure 1 is taken from Haworth's paper, and shows the total energy-distribution curve up to an energy of 35 eV. This portion of the curve was found to be nearly independent of the primary energy for primary energies greater than 37 eV.

In order to be able to derive the normal energy-distribution from the total energy-distribution, it is necessary to make some assumptions about the distribution in angle of the secondary electrons. On this point the experimental evidence is not conclusive, but it suggests that the number of secondaries emitted per unit solid angle in a direction making an angle θ with the normal is proportional to $\cos\theta$(6). This law will be assumed to be true, and it will be assumed also to apply to any fraction of the emitted electrons having total energies within any given range. The second of these assumptions is equivalent to the statement that the energy-distribution function is the same for beams of electrons emitted in any direction.

If now we suppose the number of electrons emitted, independently of direction, with energy between V and $V+dV$ to be given by

$$dN = F(V)\,dV \qquad \ldots\ldots(7),$$

then, from the cosine law, the number having total energy within this range which are emitted at angles to the normal greater than θ may readily be shown to be $dN\cos^2\theta$. Of the electrons having total energy between V and $V+dV$ these, and these only, have normal energy less than $V\cos^2\theta$. If we now write $V\cos^2\theta = U$, where U is a constant, we obtain for the number having total energy between V and $V+dV$ and normal energy less than U, where $V>U$,

$$dN\cos^2\theta = dN.U/V = U.F(V)\,dV/V \qquad \ldots\ldots(8),$$

from equation (7).

The total number having normal energy less than U and any value of total energy greater than U is found by integrating (8) from U to ∞, i.e.

$$U\int_U^\infty \frac{F(V)\,dV}{V} \qquad \text{......(9).}$$

And of course all those electrons for which $V<U$ have normal energy less than U. Adding this quantity to equation (9), we find that the total number having normal energy less than a given value U and any value of total energy is

$$\int_0^U F(V)\,dV + U\int_U^\infty \frac{F(V)\,dV}{V} \qquad \text{......(10).}$$

From this it may readily be deduced that the number N_U having any value of total energy and normal energy greater than U is given by

$$N_U = \int_U^\infty F(V)\,dV - U\int_U^\infty \frac{F(V)\,dV}{V} \qquad \text{......(11).}$$

Since N_U in equation (11) and n in equation (2) both represent the number of electrons having normal energy greater than U, the right-hand sides of these two equations must be equal, and the relation between secondary-emission coefficient and work function is given by an equation analogous to equation (4), namely

$$\delta/\delta_0 = N_\chi/N_0 \qquad \text{......(12),}$$

where χ is the increase of work function produced by a contamination.

Starting from Haworth's curve for the total energy-distribution of secondary electrons for a primary energy of 150 eV., and determining the values of the integrals in equation (11) graphically, we obtain the full curve shown in figure 2 when $\log_{10} N_U$ is plotted against U. The portion of the curve shown covers a range of 5 eV., which includes 52 per cent of the secondary electrons.

It will be observed that the curve thus obtained approximates closely to the Maxwellian form given by $\log_{10} N_U = A - bU$. The value of b which best fits the curve over the range shown is found from the slope of the dotted line in figure 2 to be 0·070 (eV.)$^{-1}$. This should therefore also be the value of b in equation (6), representing the relation between secondary-emission coefficient and work function, in the case of contaminated molybdenum. Figure 1 (b) shows a Maxwellian distribution of total energy corresponding to this same value of b. It is noteworthy that the integral of the normal energy-distribution curve approaches the Maxwellian form more nearly than does the total energy-distribution.

Deductions from the foregoing theory. The experiments to be described were carried out with the object of testing the applicability of the foregoing theory to the case of a contaminated metal surface. The following four main results are to be expected: (1) A linear relationship should exist between $\log_{10}\delta$ and χ. (2) The constant b, representing the rate of change of $\log_{10}\delta$ with χ, should have the value 0·070 (eV.)$^{-1}$ in the case of molybdenum. (3) For a given metal, the value of b should be independent of the nature of the contaminant. (4) For a given metal, the value of b should be nearly independent of the energy of the primary electrons.

§ 4. EXPERIMENTAL METHOD

In carrying out the experiments, use was made of the method of measuring secondary emission from filaments described by the author in an earlier paper⁽⁷⁾. A valuable feature of the method is that it permits of the measurement of changes in the relative contact potential of the filament whose secondary emission is being studied, with respect to a clean tungsten filament. The changes of contact potential give a measure of the changes in work function.

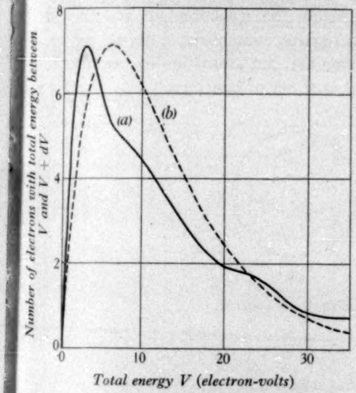


Figure 1. Total energy-distribution curves: (*a*) Secondary electrons (Haworth), (*b*) Maxwellian.

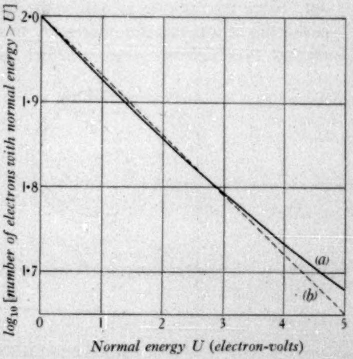


Figure 2. Integrals of normal energy-distribution curves: (*a*) Secondary electrons, (*b*) Maxwellian.

The cross-section of a typical tube is shown in figure 3 (*a*), the main dimensions being the same as those given in the paper previously referred to. The tungsten cathode C provides the primary current, T is the target (secondary-emitting) filament, and B an extra filament to provide the contamination, e.g. an oxide-coated nickel filament. This filament was maintained at cathode potential during the secondary-emission measurements.

The contact-potential measurements. The measurement of the contact potential was carried out in the following way. The cathode was maintained at a temperature such that a saturated thermionic emission current of 5 mA. was drawn to the anode and grid, when these two electrodes were at 100 volts positive potential with respect to the cathode. The target current was then measured, as a function of the target potential, with respect to the cathode, over a range of a few volts above that at which it first assumed a measurable value. The curve obtained under these conditions had a considerable linear portion, which, when extrapolated, cut the zero current axis at a point x. The difference between the value of x for the uncontaminated target and its value for any state of contamination was taken to be equal to the contact potential-difference between the clean and contaminated surfaces. It is also equal to the difference between their work functions.

It was found that the value of x obtained for any state of the target was not affected by changes of a few volts in the potential applied to the anode and grid. Any changes occurring in the contact potential-difference between these electrodes and the cathode could therefore be neglected.

The value of x obtained in this manner was referred to the potential of the tungsten cathode. In order that changes in x should give a true measure of the changes in contact potential of the target, it was necessary to ensure that the cathode was always in the same condition when the measurement was carried out. Since the cathode, as well as the target, became contaminated during the experiments, it was therefore necessary to remove this contamination by heating the cathode to a high temperature before taking each set of readings.

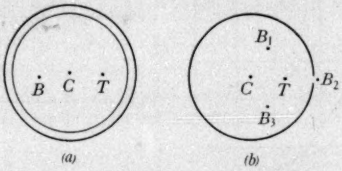


Figure 3. Cross-sections of electrode systems.

§ 5. EXPERIMENTAL RESULTS

The experimental results for films of barium on molybdenum, and of barium, thorium and oxygen on tungsten will now be presented, and a comparison of the results with the theoretical expectations will follow. An examination of some of the effects produced by comparatively thick films will then be made.

Barium (*from an oxide-coated filament*) *on tungsten*. Figure 3 (*a*) shows the disposition of the electrodes in this experiment. T was a tungsten filament 0·104 mm. in diameter and 50 mm. long, C was a similar filament 12 mm. long, and B was a nickel wire 0·18 mm. in diameter and 50 mm. long, coated with a mixture of barium and strontium carbonates in equal molecular proportions. During the pumping of the tube the filament B was heated to convert the carbonates to oxides, and eddy-current heating and barium gettering were carried out before sealing off the tube. (A slight modification of the original design, introduced during the course of the work, consisted in making the grid free to slide at one end instead of rigidly fixed. This precaution was taken to prevent distortion of the grid during the eddy-current heating.)

In carrying out the experiment, the target and cathode were first cleaned by heating at 2800° K. for a few minutes, and the contact potential and secondary-emission coefficient for 300 volts bombarding potential were measured. The result of these measurements is indicated by the point A in curve a, figure 4, which shows the relation between $\log_{10} \delta$ and the change in the work function of the target. The oxide-coated filament was then heated at about 1400° K. for a short time, and after the cathode had been cleaned the measurements were repeated. This second point is shown at B. The deposition of barium on the target from the oxide-coated filament had caused a reduction in the work function and an increase in the secondary emission. Successive repetition of these operations gave the points indicated by crosses, the final point being C.

On now heating the target at successively higher temperatures so as to re-evaporate the barium, the points marked by circles were obtained. The final condition of the target (point D) was nearly the same as its initial condition.

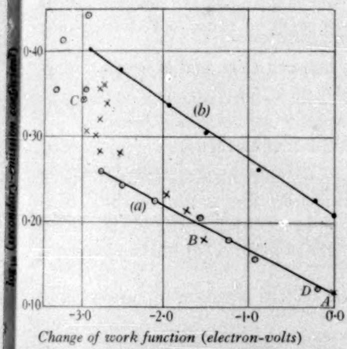


Figure 4. Relation between secondary-emission coefficient and work function: (*a*) Barium (from oxide-coated filament) on tungsten, × deposition, ⊙ evaporation. (*b*) Barium on molybdenum. Primary-electron voltage 300.

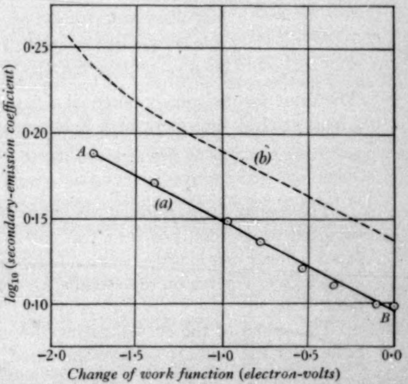


Figure 5. Relation between secondary-emission coefficient and work function for thoriated tungsten: (*a*) Author's results, (*b*) Sixtus's results. Primary-electron voltage 300.

Barium (from an oxide-coated filament) on molybdenum. This experiment was in all respects similar to that described for tungsten, except that points were obtained only during the later stages of evaporation of barium from the target. The results of this experiment, which is shown in curve b, figure 4, have already been published in *Nature*(8).

Thorium on tungsten. In this experiment the target was a thoriated tungsten filament of diameter 0·1 mm. The contaminant, thorium, was brought to the surface of the filament by diffusion from within the metal. In curve a, figure 5, the point A represents the fully activated filament. The remaining points were obtained during deactivation at successively higher temperatures. The final point B represents a clean (or very nearly clean) surface of tungsten, and it is noteworthy that the value of δ for this condition is very nearly the same as that found for pure tungsten, point *A*, figure 4 (*a*). A similar experiment has been performed by Sixtus(3), and it is interesting to compare his results, which are reproduced in curve *b*, figure 5, with the author's.*

Oxygen on tungsten. The tube used in this experiment had attached to it a side tube containing a small quantity of potassium permanganate. After measurement of the secondary-emission coefficient at a primary voltage of 300, and of the contact potential of the target, which was of tungsten, the temperature of the target was raised to 1500° K. and oxygen was admitted by heating the permanganate. After the gas had been absorbed by the getter, measurements were made on the oxygenated filament.

The following results were obtained:

For clean tungsten $\delta = 1{\cdot}31$.
For oxygenated tungsten $\delta = 1{\cdot}06$.
Change of work function on oxygenation = 1·78 eV.

The value for the contact potential difference between clean and oxygenated tungsten is in close agreement with Reimann's value of 1·75 V.(9)

§ 6. DEDUCTIONS FROM THE EXPERIMENTS

The results for barium on tungsten, barium on molybdenum, and thorium on tungsten prove that, provided that the contaminating film is not too thick, there exists a linear relationship between $\log_{10}\delta$ and χ, in accordance with the theoretical expectation. The region representing thicker films in figure 4 (*a*) will be considered later.

The slopes of the curves, giving the values of *b* in equation (6), are given in table 1 for the primary voltages indicated.

Table 1. Values (eV^{-1}) of *b* for various contaminated surfaces

Voltage (V.)	300	150	35
Barium on molybdenum	·067	·057	·050
Barium on tungsten	·052	·060	·043
Thorium on tungsten	·053	—	—
Oxygen on tungsten	·052	—	—

From these figures it is clear that for a given value of the work function and for the different contaminations on tungsten, the secondary emission is independent of the nature of the contamination. The value of *b* is found to change only to a relatively slight extent with variations in the primary voltage. The variations in table 1 are hardly outside the experimental errors.

These variations do not accord with the data given by Sixtus for thoriated tungsten(3). He found the value of *b* to fall considerably as the primary voltage was increased from 200 to 800. Thus at 400 V., for example, its value was 40 per cent lower than at 200 V. No such large variation is to be expected from the theoretical considerations brought forward earlier in this paper.

---

* The author regrets that at the time of reporting his first results to *Nature* he was not aware of the work of Sixtus.

§ 7. COMPARISON OF THEORETICAL AND EXPERIMENTAL VALUES OF *b*

It has been shown that the experimental results are concordant with the main predictions of the theory. The quantitative comparison between the theoretical and experimental values of *b* remains to be made.

The theoretical value was 0·070 (eV.)$^{-1}$ for molybdenum at 150 eV. primary energy.

An examination of the experimental data gives reason to believe that the difference between the 150-V. and 300-V. values for molybdenum shown in table 1 is fortuitous. The mean of these two values will therefore be taken as the most probable experimental value of *b* for 150-V. primaries. The value thus obtained is 0·062 (eV.)$^{-1}$, which is about 12 per cent less than the theoretical value.

It will be remembered that the theoretical value was arrived at from the slope of the line which best fitted the integrated normal-energy-distribution curve over an arbitrary range of positive energies. The experiments are concerned with the region of negative energies (as defined in § 3) covering the approximate range 0 to -3 eV. A more exact comparison of the theoretical and experimental values therefore necessitates finding the mean slope of the extrapolated curve of figure 2 over the range 0 to -3 eV. This extrapolation, though it cannot be made very exactly, yields the value 0·085 (eV.)$^{-1}$ for *b*, a value which should be nearer the truth than 0·070. With this revised value of *b*, the experimental value is 27 per cent low.

The experimental errors involved in the determination of *b* are rather large. The theoretical value involves the errors in the measurement of the energy-distribution and the error introduced by the extrapolation to negative energies. Even when all these errors are considered, however, it is difficult to account for a difference of 27 per cent.

In considering the possible causes of this discrepancy, it must be remembered that the validity of the assumption of a cosine law of distribution in angle of the secondary electrons cannot be regarded as established beyond doubt.

§ 8. EFFECTS WITH THICK FILMS

Our interest thus far has been confined to the thin-film contaminations for which the linear relationship between $\log_{10} \delta$ and χ is applicable. A special experiment was carried out with the object of investigating the thick-film region. The oxide-coated filament, previously used as a source of barium, was replaced by a nickel-barium alloy wire containing about 0·6 per cent of barium. It was hoped that the barium obtained from this source would be purer than that from an oxide-coated filament, since it is known that an oxide-coated filament gives off oxygen as well as barium, the relative amount of oxygen depending upon the amount of ageing to which the filament has been subjected, as well as on its temperature⁽¹⁰⁾.

In order to secure a fairly uniform deposition of barium over the surface of the target, three nickel-barium wires B_1, B_2 and B_3, figure 3 (*b*), were arranged symmetrically round the target *T*. To avoid undue complication the grid was omitted, the primary current calibration (required for the measurement of δ) being taken from the dimensionally similar tubes already described, in which the grid was present.

The relation between $\log_{10}\delta$, at a primary voltage of 300, and χ for this tube is shown in figure 6, which is drawn in a manner comparable with figure 4 (*a*). The portion *AB* of this curve represents the thin-film region, whilst *BC* represents the thick-film region. The thin-film portion of the curve falls along a straight line whose slope is 0·052 (eV.)$^{-1}$. It is interesting to observe that whereas the thin-film portions of the curves of figure 4 (*a*) and figure 6 have exactly the same slope, the thick-film portions are entirely different. The thick-film points lie above the linear portion of the curve for barium derived from an oxide-coated filament, and below for barium derived from a nickel-barium alloy. This difference must be attributed to the presence of oxygen, as well as barium, in the former case. This also accounts for the greater maximum reduction of work function produced when the source of the contamination is an oxide-coated filament. It may be mentioned that these differences are quite typical and have been observed with a number of different tubes.

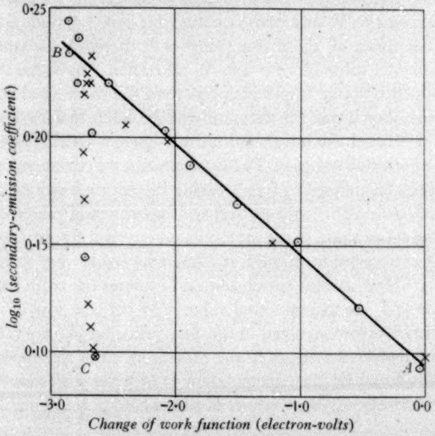


Figure 6. Relation between secondary-emission coefficient and work function. Barium (from nickel-barium alloy) on tungsten: × deposition, ⊙ evaporation. Primary-electron voltage 300.

In deriving the theoretical expression for the effect of variations of work function on secondary emission, it was assumed that the contaminating film neither absorbed primary electrons nor emitted secondary electrons. It would appear that the region *BC* in figure 6 represents thicknesses of film for which this assumption is no longer true, and that for points in this region the secondary electrons originate at least partly in the barium film itself.

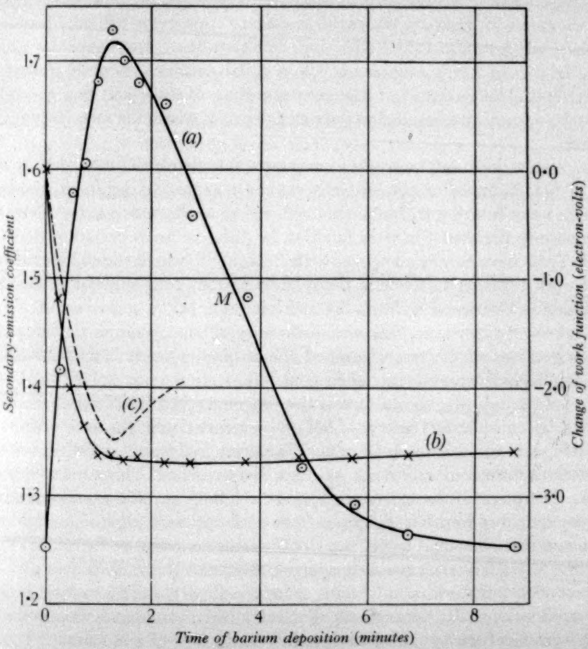


Figure 7. Variation (*a*) of secondary-emission coefficient and (*b*) of work function, with amount of barium on surface of tungsten. (*c*) Becker's work-function curve.

The data from which figure 6 was obtained are represented in a different manner by curve *a*, figure 7. This figure shows the variation of the secondary-emission coefficient with the total time of deposition of barium from the nickel-barium wires. An independent experiment showed that the rate of evaporation of barium was practically constant for the temperature and time used. Hence the time of deposition gives a measure of the relative amount of barium present on the target.

The rising portion of this curve represents the thin-film region, in which the secondary electrons originate almost entirely in the tungsten. The final portion shows a tendency for the secondary emission to approach a constant value and indicates that here the effect of the underlying tungsten is becoming negligible. In the intermediate (falling) portion of the curve the tungsten and the barium both contribute to the secondary emission.

§ 9. THE DEPTH AT WHICH SECONDARY ELECTRONS ORIGINATE

At the point *M*, figure 7, where the secondary emission is half-way between the thin-film and thick-film values (the work function being approximately constant) the secondaries probably originate in about equal numbers from the tungsten and barium films. The thickness of film corresponding to this point may therefore be taken to be approximately equal to the mean depth at which the secondary electrons originate.

An attempt will now be made to compute this depth. This may be found in terms of the thickness of film which gives the maximum thermionic emission or minimum work function (subsequently referred to as the *optimum thermionic layer*) by reference to the change in work function for different times of barium deposition, curve *b*. This curve may be compared with Becker's(11), which shows how the reduction of work function varies with the relative surface concentration of barium on tungsten. The absence of a clearly defined minimum in the author's work-function curve is probably associated with non-uniformity of the deposit, as a result of which different portions of the target attained the minimum work function at different times. In Becker's experiments such non-uniformities were probably reduced by diffusion of barium over the surface of the tungsten when the filament was heated. However, by considering the rate of fall of work function in the early stages of the deposition, it is possible to obtain a fairly accurate indication of the time at which the optimum thermionic thickness was effectively reached. This time comes out at 1·3 min. The point *M* therefore corresponds to 2·8 optimum thermionic layers.

If we can now translate depths in terms of optimum thermionic layers into depths in terms of atomic layers, we shall be able to arrive at the mean depth at which the secondary electrons originate. Unfortunately the thickness of film, or surface concentration of barium atoms corresponding to one thermionic layer, has not been experimentally determined. For caesium on tungsten the optimum thermionic layer has been found by Langmuir(12) to be 0·67 of a monatomic layer, but there is no reason to believe that the same value will apply for barium on tungsten. From theoretical considerations de Boer(13) has estimated the optimum covering for barium to be 0·29 of a monatomic layer. Perhaps the best that can be done is to take a value of 0·5 for this quantity. The mean depth at which the secondary electrons originate, according to this assumption, is 1·4 atomic layers.

A correction of this value is necessitated by the fact that the primary electrons strike the target at various angles of incidence. The mean angle of incidence, under the conditions of measurement (i.e. with target potential 300 and anode potential 450), may be taken to be the same as if the electrons remain undeviated from their rectilinear paths by the presence of the target; its value is therefore about 30° to the normal. On the basis of Bruining's work⁽²⁾ on the effect of angle of incidence on the mean depth at which secondary electrons are liberated, the depth for normal incidence will thus be increased by the factor sec. 30° compared with the depth for 30° incidence. The application of this correction to the value obtained above gives 1·6 atomic layers for the mean depth at which the secondary electrons originate, with a primary voltage of 300 and normal incidence. This figure may be in error by a factor of about 2, on account of the uncertain value of the optimum thermionic layer.

From his experiments Bruining⁽²⁾ has calculated the product of the absorption coefficient for secondary electrons in nickel and the mean depth at which they originate to be 0·45 for 300-V. primary electrons. He then substitutes Becker's value⁽¹⁴⁾ of $1{\cdot}5 \times 10^6$ for the absorption coefficient for electrons of energy equal to the mean energy of the emitted secondaries, and obtains the value 30 angstroms for the mean depth at which the secondary electrons originate. This figure, which represents about 14 atom-layers of nickel, is of a different order of magnitude from that found in the present work.

§ 10. OTHER WORK ON COMPLEX SURFACES

It has been shown in § 6 that the effect of a change of work function on the logarithm of the secondary-emission coefficient is nearly independent of the energy of the primary electrons. On this basis it is possible to describe qualitatively how the shape of the curve representing the logarithm of the secondary-emission coefficient as a function of the primary energy will be affected by the deposition on a metal surface of increasing quantities of a contaminant.

So long as the contamination satisfies the thin-film criterion the change of secondary emission will be determined solely by the change in work function, hence the change in log δ will be the same for all values of the primary energy. In this region, therefore, the successive degrees of contamination will be manifested by a displacement of the original curve parallel to the axis of log δ, without alteration of shape. When the thickness of the film becomes sufficient for the effect of the underlying metal to be neglected, a curve will be obtained representing simply the secondary emission of the contaminant in bulk. In the intermediate region, between the thin and very thick films, the shape of the curve will, in general, differ from that for either of the simple materials.

These expectations are substantially verified by the experimental curves of Copeland⁽¹⁵⁾ showing the logarithm of the secondary-emission coefficient, as a function of the primary voltage, for a metal on which were deposited successive amounts of a contaminant. In each of the three cases studied, the first effect of the contamination was to displace the curve parallel to the axis of log δ. Thus, in the case of aluminium contaminated with platinum a reduction of $\log_{10} \delta$ by about 0·15 took place before the shape of the curve became definitely changed. Since the work function of platinum is higher than that of aluminium, a reduction in log δ would be expected as a result of the deposition of the former metal on the latter. An opposite effect was observed when calcium was deposited on gold; this again is to be expected from consideration of the work function.

Since the thickness of film for which the simple work-function effect ceases to apply is related to the depth at which the secondary electrons are liberated, and since this depth increases with the energy of the primary electrons, it would be expected that the shape of the curve typical of the underlying metal would persist to a greater thickness of film at the higher than at the lower primary energies. This expectation also is borne out by Copeland's results.

Whilst Copeland's interpretation of his experiments is concerned chiefly with what has been described in the present work as the "thick-film" region, it seems that his generalization to the effect that the major portion of the observed changes in secondary emission must be ascribed to some other cause than the variation of work function tends rather to underestimate the importance of a factor which has considerable significance in any interpretation of phenomena of this kind.

§ 11. THE SIGNIFICANCE OF THE WORK-FUNCTION EFFECT

The general result of the investigation which has been described may be stated in the following terms: *For any metal whose work function is varied by the deposition on its surface of a thin film of a foreign substance, changes in secondary-emission coefficient are determined solely by the accompanying changes in work function. The magnitude of such changes can be predicted if the energy-distribution of the secondary electrons is known.*

There is no reason to doubt that this law can be generalized to include non-metals as well as metals. On the other hand, it does not account for the changes in secondary emission produced by a thick-film contamination, neither does it give any information about the relative secondary-emission coefficients of different specific materials.

The following discussion, which is admittedly speculative, suggests how the knowledge already gained may be brought to bear on the problems raised by some of the highly complex secondary-emitting materials referred to in § 1.

We may begin by considering what is the maximum secondary emission obtainable from a simply-contaminated metal. The secondary-emission coefficient which would be given by tungsten, for 300-V. primary electrons, if its work function were imagined to be reduced to zero by a thin-film contamination would be 2·3, and that for molybdenum under the same conditions would be 2·9. From the knowledge that the energy-distribution curves for secondary electrons for the dozen or so metals that have been studied in this respect are all quantitatively similar, combined with the fact that the range in the secondary-emission coefficients of the clean metals which have been reliably examined is not very great, it is possible to predict that the highest secondary-emission coefficient obtainable from any metal having a thin-film contamination will not be much more than 3·0 at 300 volts, however much its work function is reduced.

It is known that a number of complex substances yield secondary-emission coefficients much in excess of this value. As a typical case caesium on caesium oxide on silver, referred to in § 1, may be cited. The secondary-emission coefficient for this material at 300 V. may be as high as 8·0. There is nothing in the preceding work which gives any hint of the reason for such a high value.

If, however, we regard the material as a thin-film contamination of caesium on caesium oxide, and if we assume that the uncontaminated caesium oxide would have a very much higher work function than the activated surface, there are two interesting possibilities. It may be (*a*) that the secondary-emission coefficient for the uncontaminated caesium oxide is about the same as that for a metal having the same work function, but the rate of change of secondary-emission coefficient with work function is much greater; or (*b*) that the rate of change of secondary-emission coefficient with work function is about the same as for a metal, but the secondary-emission coefficient for the uncontaminated caesium oxide is very much greater than that for a metal having the same work function. (*b*) is unlikely to be true, since no oxides in the uncontaminated state have been reported as having very much higher secondary-emission coefficients than the pure metals. If, however, (*a*) is true, it follows that the average energy of the secondary electrons from caesium oxide is very much lower than that of the secondary electrons from a metal. This is a matter which could be investigated experimentally.

§ 12. ACKNOWLEDGEMENT

The author desires to tender his acknowledgement to the Marconiphone Company and the General Electric Company on whose behalf the work was done which has led to this publication.

REFERENCES

(1) Penning, F. M. and Kruithof, A. A. *Physica*, 'sGrav., **2**, 793 (1935).
(2) Bruining, H. *Physica*, 'sGrav., **3**, 1046 (1936).
(3) Sixtus, K. *Ann. Phys.*, Lpz., **3**, 1017 (1929).
(4) Haworth, L. J. *Phys. Rev.* **48**, 88 (1935).
(5) Haworth, L. J. *Phys. Rev.* **50**, 216 (1936).
(6) Farnsworth, H. E. *Phys. Rev.* **31**, 414 (1928).
(7) Treloar, L. R. G. *Proc. phys. Soc.* **48**, 488 (1936).
(8) Treloar, L. R. G. *Nature*, Lond., **137**, 579 (1936).
(9) Reimann, A. L. *Phil. Mag.* **20**, 594 (1935).
(10) Reimann, A. L. *Thermionic Emission*, p. 193 (1934).
(11) Becker, J. A. *Trans. Faraday Soc.* **28**, 148 (1932).
(12) Langmuir, I. *J. Amer. chem. Soc.* **54**, 2798 (1932).
(13) de Boer, J. H. *Electron Emission and Adsorption Phenomena*, p. 104 (1935).
(14) Becker, J. A. *Ann. Phys.*, Lpz., **2**, 249 (1929).
(15) Copeland, P. L. *Phys. Rev.* **48**, 98 (1935).

DISCUSSION

Dr J. E. R. Constable. I should like to ask whether the magnitude of the work function appreciably affects the number of incident electrons which penetrate the target surface and, if so, whether the author has allowed for this effect.

Author's reply. If potentials are referred to the cathode, a change in the work function of the target will alter the effective potential outside the metal (i.e. in the vacuum) but not that inside. Owing to the former effect the primary current may be changed by a maximum amount of 0·5 per cent at a primary energy of 300 V., but this has been neglected. Since the potentials within the metal are unaffected, there will be no change in the energy of the primary electrons which penetrate the surface of the target.

THERMIONIC APPROXIMATIONS TO THE GAS-COVERED FRACTION OF AN ADSORBING SURFACE, APPLIED TO THE TEMPERATURE DEPENDENCE OF OXYGENATION AND OXIDATION OF A TUNGSTEN FILAMENT

By M. C. JOHNSON, M.A., D.Sc., Physics Department,
University of Birmingham

AND

F. A. VICK, Ph.D., University of London, University College,
formerly of the University of Birmingham

Received 19 *September* 1936. *Read* 23 *April* 1937

ABSTRACT. A distinction is made between two methods of using thermionic data to estimate for a filament surface the fraction which is covered with oxygen. Conditions are formulated under which either of the two gives approximations to the true fraction defined by concentration of particles in an adsorbed layer. In the method depending upon work functions the necessity for obtaining true instead of apparent thermionic constants for a composite surface is introduced, as these are found to differ widely for oxygenated tungsten. A set of experimental data is analysed by means of the two methods in turn, and empirical graphs are thence obtained representing approximately the temperature variation of the gas content of the surface. The limiting slopes to which these graphs tend in the valid portions of their respective ranges agree with the temperature coefficients of oxidation and oxygen evaporation known from other experiments.

§ 1. INTRODUCTION

In the physics and chemistry of composite surface layers, the fundamental variable is the fraction of surface which is occupied by any given component or which conforms to any given condition. This fraction, written θ in most of the literature, has been estimated in restricted cases only, notably the condensation of alkali vapours upon a refractory metal such as tungsten to which they are electropositive and whose thermionic emission they greatly increase. To determine θ thermionically for the case of an electronegative gas such as oxygen involves considerably greater difficulty, and has mainly been attempted through its intermediate action in cementing more electropositive materials to the underlying metal. In the course of experiments on reactions at a tungsten surface in oxygen at pressures below 10^{-3} mm. of mercury, it was found necessary to reconsider the relation of θ to observable quantities. The results, with their application to the temperature variation of adsorption and oxidation, are presented here. It should be understood that the data are simply saturated thermionic currents obtained with appropriate precautions in the presence of controllable traces of oxygen too small to involve ionization by collision. In addition to the usual pretreatment of all metal surfaces, high-frequency degassing, baking of walls, etc., and the isolation of an isothermal length of filament by means of guard rings, these precautions included technique for maintaining constancy of very small gas pressures over long periods; details may be found in some already published papers(1) on certain other problems for which the experiments were designed.

§ 2. EXPERIMENTAL METHODS FOR OBTAINING AN APPROXIMATION TO THE FRACTIONS OF SURFACE COVERED

In problems in which θ is to be a variable in thermodynamic or chemical equations, its appropriate definition is

$$\theta = N/N_1,$$

where N is the number of gas particles of any one kind per unit area on the surface and N_1 is that number at saturation of the layer. With this definition a plot of $\log_e\{\theta/(1-\theta)\}$ against $1/T$ would express by its slope an energy of adsorption or of surface reaction, in the manner familiar in studies of three-dimensional gas behaviour.

But since no means exists for counting the particles which remain on the surface and so correlating N directly with the accompanying physical changes, an approach must be made to θ through some experimental quantity θ_x to be chosen as follows. (*a*) θ_x must be unambiguously accessible through some observable property of the material. (*b*) Whatever the significance chosen for x, the limits $\theta_x = 0$, $\theta_x = 1$ must denote respectively the state of bare metal and of complete gas covering, satisfactorily related to some chemical or physical criterion of saturation. (*c*) The temperature dependence of θ_x must follow as closely as possible that of N/N_1. For thermionic approaches to θ the chosen indicator must be the simplest function of emission current i consistent with the above conditions, so that

$$\theta_x = f(i)$$

and

$$0 < \theta_x < 1.$$

The requirement (*c*) essentially precludes any one form of θ_x from being used over more than a portion of the range $\theta = 0$ to $\theta = 1$, since any simple function which follows the course of N/N_1 when the adsorbed particles are widely separated will fail to do so when they are so closely packed as to influence each other. Hence any variation of $\log_e\{\theta_x/(1-\theta_x)\}$ which is linear for sparse surface concentrations will become curved before the layer approaches saturation. We proceed to consider two such forms of θ_x, or model approximations to θ.

(A). If the lateral components of the fields of force surrounding adsorbed particles diminish so rapidly with distance that the effects of any local deposit may be considered to cease abruptly at its edge, the whole surface may be regarded as divided into elementary areas of two kinds, whose electron-emitting properties are those of completely bare and completely gas-covered metal respectively. Using the

Richardson equation, with emission constants A_1 for bare and A_2 for covered surface, and work functions ϕ_1 for bare and ϕ_2 for covered surface, we have

$$i_\theta = A_1 T^2 e^{-\phi_1/\kappa T} (1-\theta_x) + A_2 T^2 e^{-\phi_2/\kappa T} (\theta_x) \qquad \ldots\ldots(1).$$

If, for comparable values of θ_x and $1-\theta_x$, the first term is large compared with the second term, we have approximately

$$i_\theta = i_0 (1-\theta_x) \qquad \ldots\ldots(2),$$

whence θ_x can be found directly. We adopt the notation θ_d for this particular instance of a θ_x, determined by current deficiency so that

$$\theta_d = i_0 - i_\theta / i_0 \qquad \ldots\ldots(3).$$

For the highly electronegative deposits with which we deal, the condition $i_0 \gg i_1$ is fulfilled, oxygen reducing the emission from tungsten to about 10^{-4} of its clean value; for a layer of an electropositive element such as caesium, which greatly increases instead of decreasing the emission, a corresponding θ_x would be based on the approximation

$$i_\theta = i_1 \theta_x.$$

(B). If the adsorbed particles modify the field over the whole surface while the layer is still very unsaturated, there is strictly no region behaving as a clean surface, and the whole area may be regarded as altering its properties homogeneously according to the growth of mean surface density of adsorbed material. On this view θ_x is not so much a fraction of area as a measure of partial acquisition of a certain property ascribable to the surface as a whole. The equations of paragraph (A) could not then be used unless an inconveniently large number of terms were introduced, with values of A and ϕ intermediate between those for clean and covered metal.

This second instance of a θ_x accordingly appears as a fractional difference in the work done in emission over the whole surface, and we adopt the notation θ_w, so that

$$\theta_w = (\phi_\theta - \phi_0)/(\phi_1 - \phi_0) \qquad \ldots\ldots(4).$$

The form in which this definition has been used by Langmuir and others may be seen by substituting in the Richardson equation at constant temperature, obtaining

$$\theta_w = (\log i_\theta - \log i_0)/(\log i_1 - \log i_0) \qquad \ldots\ldots(5).$$

Equation (5) is valid only if A is constant or if $\log A$ is proportional to ϕ.

θ_w has been used in studying the deposition of alkali vapours, where i_1 is large and easily determined. The extremely minute and uncertain values of i_1 for electronegative layers has hitherto prevented its application to these. This difficulty is escaped only when (as in one of our previous papers) i_1 can be eliminated by isothermal observation at two different values of θ.

In general θ_w will more nearly approximate to the true θ, or N/N_1, for widely distributed or laterally mobile layers, since they conform more nearly to the physical requirements of paragraph (B), whereas θ_d will follow θ for immobile material sparsely distributed. Adsorbed vapours consisting of strongly dipolar molecules or inert ions will possess the long-range fields assumed for θ_w, while the short-range fields surrounding neutral atoms will allow the assumptions for θ_d to be more nearly correct. These considerations make it clear that neither θ_w nor θ_d bear the same relation to N/N_1 for large as for small values of θ. In particular the contribution made by each additional adsorbed particle to modifying the electronic work function has been shown by several workers to vary with mutual depolarization of neighbours in the surface layer; any such interaction with neighbours will also cause the work of evaporating a neutral particle from the surface to vary with packing of the adsorbed material.

§ 3. θ_w FOR TRUE WORK FUNCTION AND APPARENT WORK FUNCTION

The sensitiveness of θ_w to the value assumed for i_1 in equation (5) shows that this method of approximating to θ requires a reliable estimate of the emission constants of the fully covered metal. For the particular interface with which our experiments deal the term OW has been used by most writers, without prejudice to the chemical state of the oxygen covering so long as the latter is regarded as complete, so that $\theta = 1$. Kingdon(2) attempted to determine these constants for OW by experiments in which gas was admitted to the hot tungsten filament at a rate sufficient to compensate for oxidation, and his values $A_{OW} = 5 \times 10^{11}$ A./cm.^{2} and $\phi_{OW} = 9{\cdot}2$ eV. have been widely quoted. Subsequent work, however, has thrown serious doubt on the possibility either of attaining the condition $\theta = 1$ at any high temperature in the presence of gas, or even of keeping θ at any constant value over a temperature range, during rapid oxidation, while Fowler(3) and others have shown the inherent improbability of Kingdon's value of A_{OW} as a genuine thermionic constant. It is generally agreed that A_{OW} is more likely to be equal to or even less than the A_W measured with clean metal, about 10^2 A./cm.^{2}; the form of Richardson's equation then shows that observed values of emission demand a much lower value of ϕ_{OW} than that offered by Kingdon. A more reliable way of estimating ϕ_{OW} is due to Reimann's careful and repeatable measurements of the contact potential-difference between OW and W, since a contact potential represents, to a first approximation, the difference between the values of ϕ for adjacent surfaces. ϕ_{OW} is thus obtainable by adding Reimann's potential to the ϕ for clean tungsten, the result being $6{\cdot}35$ eV. Reimann has shown(4) that a quantity of this order can account satisfactorily for the actual small emissions if A is the same for OW as for W. Since the contact measurements do not involve the above-mentioned temperature control of θ they are free from the objection that applies to Kingdon's experiments, and can replace the latter as the source of ϕ_{OW}.

We have, in the last of the publications referred to, investigated the new interpretation of currents from partially oxygenated tungsten necessitated by the above considerations, and we summarize as follows the portions of our argument relevant to the present need for deducing θ_w.

Consider the Richardson plots typified in figure 1, in which the slope of log i/T^2 against $1/T$ determines ϕ, while the vertical intercept at zero abscissa is measured to obtain log A. The line bc for a fully oxygenated surface would, if obtainable, lie below the line *bd* for clean tungsten, and the vertical intercept of *bc* would be either identical with or less than that of *bd* since the adsorbed oxygen cannot increase emission. But if a trace of oxygen, even below 10^{-6} mm., is present while the readings for the Richardson plot are being obtained, the observed currents will distribute themselves over a transition plot typified by the broken curve which intersects in turn the several true Richardson lines, shown dotted, for $\theta_w = 0{\cdot}1$, $0{\cdot}2$, etc., in the area between the lines *bd* ($\theta_w = 0$) and *bc* ($\theta_w = 1$). The course of this transition curve depends upon the rates of adsorption, evaporation, oxidation, etc., which determine the rate of passage from $\theta = n$ to $\theta = m$, where n and m are any fractions. So long as it is impossible to make θ equal to 1 to a higher accuracy than that which, in view of the rapid volatilization of oxide, is available in practice, a nearly linear portion of an observed plot does not yield any true ϕ and A but only apparent constants; these may be considerably in excess of even the true values for the fully oxygenated metal, being merely tangents to some portion of the transition curve. By a series of measurements of pressure and temperature we have proved in detail that the data usually quoted from the work of Kingdon belong to this category of apparent ϕ and A.

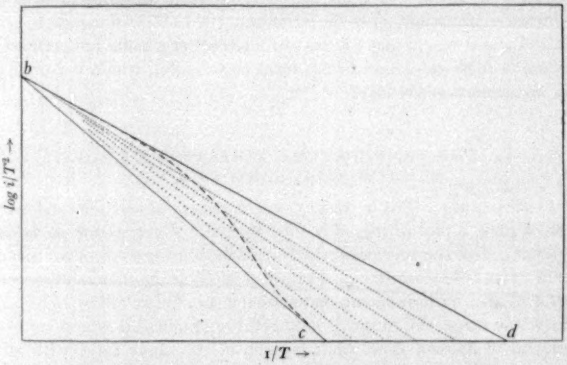


Figure 1. Transition curve between Richardson plots.

To determine a set of values of θ_w, we draw on a large scale a diagram such as that typified in figure 1, inserting all our experimental curves. First the line corresponding to *bd* is obtained from our measurements in the highest vacuum and agrees with the standard determinations of A_W and ϕ_W. Secondly, that corresponding to *bc* is fixed by making a line whose slope gives $\phi_{OW} = 6{\cdot}35$ meet *bd* at $1/T = 0$, thus fulfilling the two consequences of accepting Reimann's contact potentials and the magnitudes of observed emissions.

It is to be noticed that temperature-dependence of any true work function is essentially a second-order correction as compared with the difference between these apparent and true functions, and is neglected throughout, so that all true Richardson plots are taken as straight and only the transition plots as curved.

The diagram fulfils the conditions under which our equation (5) is equivalent to equation (4), so the Richardson plots for various values of θ_w between 0 and 1 will lie between *bc* and *bd*, as dotted in figure 1. These are inserted in the large working graph by geometrical construction, slopes for $\theta_w = 0{\cdot}1, 0{\cdot}2$, etc. being obtained from the slopes for the work functions $\phi_{OW} = 6{\cdot}35$ and $\phi_W = 4{\cdot}64$ by the relationship of equation (4). For any observed current and temperature, $\log i/T^2$ and $1/T$ then constitute a pair of coordinates determining some particular θ_w as they meet on some particular line intermediate between *bd* and *bc*.

Any other mode of deducing ϕ_{OW} would of course expand or contract the scale of the θ_w thus obtained, but it is clear that no such amendment from thermal measurements is admissible, since the latter only yield a transition plot; in particular, Kingdon's A and ϕ would make *bc* and *bd* intersect at a finite temperature, giving larger emission from gas-covered than from clean metal, which is contrary to the nature of an electronegative layer.

§ 4. THE TEMPERATURE VARIATION OF $\theta/(1-\theta)$ FOR EACH FORM OF θ_x

By the ordinary arguments in the physical chemistry of reactions and the physics of change of state, a plot of $\log_e \{\theta/(1-\theta)\}$ against $1/T$ represents in its slope the energy exchanged in the processes which contribute to growth of θ. Since this is only true in so far as θ measures actual values of N/N_1 or the fractional concentration of deposit, and since we have shown that neither θ_d nor θ_w can follow N/N_1 accurately over their whole range, the energy is only reliably obtained if inferences from each approximation in its own appropriate portion of the range agree with inferences from other experiments. Accordingly we plot in figure 2 this temperature dependence of θ_d determined by inserting the data in equation (3), and also the temperature dependence of θ_w obtained from the same data by the method of evaluating θ_w explained in the preceding section; in each instance three typical sets of measurements are used, curves 15, 19, 17, corresponding to highest, medium, and lowest gas pressures respectively, all at oxygen pressures between 10^{-3} and 10^{-5} mm.

From our physical theory of θ_d and θ_w, it is to be expected that the course of the former will tend more nearly to agree with that of θ itself at the lowest pressures and highest temperatures, i.e. at the smallest values of θ, since a very sparsely separated distribution of adsorbed particles will be unable to affect the large uncovered areas between; but as θ grows the tendency will be for θ_w to represent the molecular state of surface more nearly, as the whole area will become affected by overlapping fields. Hence the portions of these experimental graphs likely to afford the most reliable information as to the temperature dependence of θ or N/N_1 are *AB* and *CD*, where high temperature and low pressure support the approximation θ_d and low temperature and high pressure support the approximation θ_w respectively. Owing to this way in which the temperature and pressure variables combine there is no advantage in attempting to join θ_a and θ_w into a single curve for any given pressure, and we only regard as significant the maximum slope of the one and the minimum slope of the other, since that is where their respective underlying assumptions tend to be fulfilled; numerical comparison between values of θ_a and of any θ_w obtained by any method of estimating i_1 shows that for given pressure and temperature the two approximations to θ may differ widely in absolute magnitude. But since θ is of importance in its temperature coefficient rather than its magnitude at any point, there is no need to do more than compare the slopes at A and D. This will be of interest as comparing the temperature dependence of gas-concentration in very sparse and in very dense adsorbed layers respectively, and can be related as follows to facts previously known concerning the energy needed to remove oxygen in various forms from tungsten.

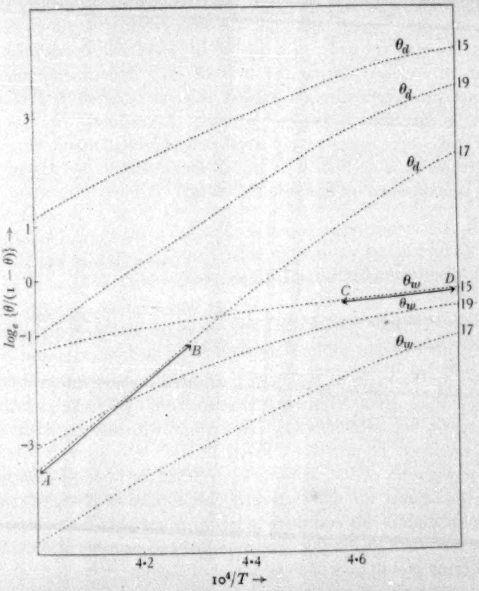


Figure 2. Temperature dependence of surface covering.

§ 5. COMPARISON WITH OTHER EXPERIMENTS

AB and CD are selected not only because each approaches the behaviour of a genuine θ, but also because under the same two extreme sets of conditions the complex action of oxygen on tungsten approaches to the simple states commonly distinguished as "oxygenation" and "oxidation" respectively; the slopes intermediate between AB and CD represent not merely the failure of θ_d and θ_w to follow θ from zero to unity, but also the merging of the temperature dependence of adsorption at small θ into the different temperature dependence of chemical reaction at large θ. For this general reason the graphs would exhibit curvature even if θ were correctly obtainable over the whole range.

Since this chemical reaction at the surface results in slow disappearance of pure metal and pure gas, a tungsten-oxygen interface is not completely described by reversible processes. Hence, although the repeatability of our observations and their independence of the order of sequence indicates that every value of θ and of pressure can be steadied during the time of each experiment, nevertheless no simple balance can represent the complete relation between θ, T and pressure p or number ν of gas impacts per cm.^{2} per sec. Accordingly any isotherm of the Langmuir-Frenkel type suited to any small range of θ will merge into another with a different temperature coefficient in any adjacent range. Let any such restricted equilibrium be expressed by Langmuir's relation

$$\theta = \frac{\alpha\nu}{1+\alpha\nu},$$

$$\frac{\theta}{1-\theta} = \alpha\nu.$$

Let a temperature dependence be added,

$$\alpha = Ce^{E/\kappa T};$$

E calories per mol. represents the energy required for any action resulting in loss of oxygen from the surface. This was first introduced by Frenkel, but the generality of its present definition precludes our identifying C with any particular time interval such as that originally postulated by Frenkel.

This generalization of the well-known grounds for obtaining E from the slope of log $\{\theta/(1-\theta)\}$ against $1/T$ will then refer only to that small region over which the restricted equilibrium holds and there is reason to suppose that a fixed E is applicable; outside each such region E will be modified and possibly also the function of ν as in the different power laws of Fowler and of Roberts.

Two such quantities E, controlling the loss of oxygen from tungsten, are known from measurement, although different authors give different molecular and atomic explanations of them. (*a*) At the lowest gas pressures oxygen is always found to be very strongly attached to the pure metal and slow to evaporate, the E being given by Langmuir and Villars(5) as 162,000 cal., by the present authors(6) as 147,000, and by Roberts(7) as of the order of 130,000. (*b*) At higher pressures a rapid oxidation is always found to set in, WO_3 evaporating readily as fast as it is formed: using some experiments of Langmuir, Rideal and Wansbrough-Jones(8) have estimated the energy required for activation to this more volatile state as 20,000 cal., and on different assumptions we have used the same data to obtain 25,000. Hence the mode of escape of oxygen from tungsten, in opposition to the growth of θ, ranges from the evaporation of an oxygenation layer requiring about 150,000 cal. for its removal, to the instant removal of an oxide layer requiring about 20,000 only for its formation, each of these E's being experimentally defined by an observed temperature coefficient. Hence the slope of our graph of log $\{\theta/(1-\theta)\}$ plotted against $1/T$ should reach approximately 150,000 at $\theta \to 0$ and $\nu \to 0$ and 20,000 when θ and ν become large. These are the two regions AB and CD respectively in figure 2, where θ_d and θ_w each in turn attains some validity as an approximation to the behaviour of θ.

Measurement of figure 2 yields 160,000 and 20,000 as limiting slopes under these two conditions, suggesting that although these thermionic methods may give absolute values of θ much in excess or defect of actual gas concentration, their temperature variation is correct within the accuracy of experiment in those regions where each approximation in turn becomes valid.

§ 6. CONCLUSION

A set of thermionic currents from tungsten, measured in the presence of very small and approximately constant traces of oxygen, can be analysed in two ways for obtaining information as to θ, the fraction of surface covered. Of the current-deficiency approximation θ_d and the work-function approximation θ_w the former is more capable of expressing a correct course of the way surface conditions vary at high temperature and low gas pressure, and the latter at low temperature and high gas pressure. After devising a new method for obtaining the work functions of a partially oxygenated surface, we have plotted a graph of log $\{\theta/(1-\theta)\}$ against $1/T$ for three gas pressures according to each of the two approximations θ_d and θ_w. Measurement of the low-temperature, high-pressure and high-temperature, low-pressure extremes of the graphs yields temperature coefficients corresponding to 160,000 cal. and 20,000 cal. respectively, from the slopes to which they tend where the above conditions for the validity of each approximation in turn is fulfilled. These values agree with the high energy of oxygen evaporation and the low energy of oxidation, previously estimated as from 130,000 to 162,000 and 20,000 or 25,000 respectively.

§ 7. ACKNOWLEDGEMENT

We are very grateful to Prof. S. W. J. Smith, F.R.S. for his kindly provision of all facilities for this work.

NOTE ADDED 15 MARCH 1937

When the concentration of a deposit is such as to justify the common term "film", however dilute, θ_w is the more reliable approximation to N/N_1. But when the adsorbed atoms are so few and widely separated that the regions not contributing to clean emission are isolated, θ_d is the more reliable, as it is not possible to average the work function over such a discontinuous surface.

Since there is no direct evidence as to the concentration at which θ_w supersedes θ_d for the case of OW, our curves are not claimed as independent data for determining E. If θ_w were valid throughout all concentrations, our slope would give the

E of evaporation as 110,000 and the *E* of oxidation as 20,000, while if θ_d were valid throughout the slope would give 160,000 and 35,000. But as there is independent evidence that these quantities are not far from 150,000 and 20,000 respectively, our results may be taken as indicating that the temperature coefficient of θ_d is a fair approximation under just those conditions that give 160,000, while the temperature coefficient of θ_w is preferable under the conditions that give 20,000.

REFERENCES

(1) Johnson and Vick. *Proc. roy. Soc.* A, **151**, 296 and 308 (1935) and **158**, 55 (1937).
(2) Kingdon. *Phys. Rev.* **24**, 510 (1924).
(3) Fowler. *Proc. roy. Soc.* A, **122**, 44 (1929).
(4) Reimann. *Phil. Mag.* (7), **20**, 594 (1935).
(5) Langmuir and Villars. *J. Amer. chem. Soc.* **53**, 486 (1931).
(6) Johnson and Vick. *Proc. roy. Soc.* A, **151**, 313 (1935).
(7) Roberts. *Proc. roy. Soc.* A, **152**, 467 (1935).
(8) Rideal and Wansbrough-Jones. *Proc. roy. Soc.* A, **123**, 202 (1929).

DISCUSSION

L. R. G. Treloar. The paper gives no information concerning a problem of very considerable physical interest, namely, the way in which the work function varies with the actual number of oxygen atoms present on a tungsten surface, i.e. with the true value of θ. Equation (4) defines a surface covering θ_w such that the relation between ϕ and θ_w is linear. Now in the case of electropositive contaminations, for which the true relation between ϕ and θ is known, it does not even approximate to linearity. For the case of oxygenated tungsten it seems not unlikely that there may be a similarly wide departure from linearity. If this is so, it seems at first sight rather strange that the application of equation (4), even over a small range of θ, should lead to the correct value of the energy associated with the oxidation process.

Authors' reply. The solution of Mr Treloar's problem would constitute a great advance in the subject, but the title of our paper implies correctly that it lies outside our present purpose. We have explained in § 2 that this is because no reliable method yet exists for counting the oxygen particles on the surface as has been done for alkalis: electropositive experiments can be carried out far below the condensation temperature of the alkali vapours involved, but for oxygen the latter is less accessible. Thus even a molecular-ray method cannot decide with precision how many particles have reached the filament and how many remain there. Hence at present the only access to θ with oxygen is through these approximations, for whose validity the correct value of the energy-slope affords some support. Actually, since the departure from linearity of ϕ/θ for alkalis is due to cohesion between the adsorbed particles, this is not to be expected to the same extent with oxygen, which binds more to the tungsten and less to itself. At larger values of θ than we ourselves use, other breakdowns of the relation occur which, however, do not concern the subject-matter of this paper.

THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF A SAMPLE OF ACHESON GRAPHITE FROM 0° C. TO 800° C.

By R. W. POWELL, B.Sc., Physics Department, National Physical Laboratory, Teddington

Received 5 *February* 1937. *Read* 23 *April* 1937

ABSTRACT. Determinations have been made of both the thermal and the electrical conductivities of a sample of Acheson graphite over the temperature-range from 0° C. to 800° C. The thermal conductivity K is found to decrease from a value of 0·40 unit at 0° C. to 0·16 at 800° C., the rate of decrease being greater at lower temperatures. The electrical conductivity σ has at 0° C. a value of 1218 Ω^{-1}-cm^{-1}, which increases to a maximum value of 1518 at 450° C. and decreases to 1444 at 800° C. The corresponding Lorenz function $K\sigma^{-1}T^{-1}$ has a value of 121×10^{-8} at 0° C., which is more than 200 times the value indicated by the electronic theory and possessed by most well-conducting metals. With increase in temperature the value of the Lorenz function decreases rapidly, its value being given by the equation $K\sigma^{-1}T^{-1} = 0{\cdot}0294T^{-1{\cdot}8}$. Thus the Wiedemann-Franz-Lorenz law does not hold for the present sample of graphite, but is replaced by the equation $K\sigma^{-1}T^{0{\cdot}8} =$ a constant. The power to which the absolute temperature is raised is different, as well as the constant value of the expression.

§ 1. INTRODUCTION

In an earlier paper(1) values have been published for both the thermal conductivity K and electrical conductivity σ of several heat-resistant alloys. Some of these values showed considerable departures from the Wiedemann-Franz-Lorenz law, according to which $K\sigma^{-1}T^{-1}$ is constant. The greatest departure occurred at 0° C. where, for two of the metals tested, the value of the Lorenz function was about double that indicated by the electronic theory and possessed by most good conductors. The extent of the deviation decreased with increase in temperature.

Graphite has a thermal conductivity of the same order as that of many metals, yet according to Koenigsberger and Weiss(2), Barratt(3) and Störmer(4), its Lorenz function in the neighbourhood of room-temperature is some 200 to 400 times as great at the normal value. It was considered of interest to ascertain whether the extent of this deviation would also decrease with increase in temperature, and for this purpose determinations of the thermal and electrical conductivities have now been made on a sample of Acheson graphite over a range of temperature similar to that covered by the earlier experiments.

§ 2. EXPERIMENTS

The graphite selected for use in this investigation was a sample of Acheson graphite which was originally in the form of a rod some 9 cm. in diameter and 75 cm. long. From this sample a specimen 7·34 cm. in diameter and 38 cm. long was prepared. This was first tested over the temperature-range from 30° C. to 200° C. by a method similar to that already described for the heat-resistant alloys(1).

The rod was mounted vertically within a coaxial cylindrical guard tube, and the interspace was packed with heat-insulating powder. The lower end of the rod was electrically heated, and the temperature-gradient established in the rod in the final matched steady state was measured by means of thermocouples. The heat flowing along the rod was measured by means of a water-flow calorimeter attached to the upper end, the thermal contact between the graphite and the calorimeter being improved by means of a small mercury bath.

The rod of graphite was later turned down to a smaller diameter of 3·85 cm. and the thermal-conductivity measurements were repeated. For this smaller size of rod a water-flow calorimeter was used which consisted of a coil of tubing soldered to a slightly tapered brass tube about 10 cm. in length and 3·8 cm. in maximum diameter. This unit made good contact with a similar taper on one end of the graphite rod. The values of the thermal conductivity obtained for both sizes of rod are plotted in figure 2, and it will be seen that the two sets of data are in close agreement. The specific resistances also of the two rods agreed. These were measured by the usual method in which the fall in potential along a length of the rod was compared with that across a shunt of known resistance when the same current was passed through each.

To extend the measurements to higher temperatures it was necessary to use an evacuated enclosure to prevent oxidation of the specimen. For these tests the rod 3·85 cm. in diameter was further machined to have a diameter of 1·47 cm. A 20-cm. length of this thin rod was first tested in an apparatus which formed part of an exhibit at the Physical Society's twenty-fifth annual exhibition of scientific instruments and apparatus, and which was subsequently illustrated and described in a published account of the exhibition(5).

The energy input to a platinum heating coil wound on a steatite former and enclosed in an axial hole in the top of the graphite rod was measured. Lateral loss of heat was prevented by the usual matched-guard-tube method, and loss in an upward direction was prevented by mounting a guard heater above the top of the rod and guard tube, and adjusting its energy until a thermocouple located between this heater and the top of the specimen indicated the same temperature as did thermocouples pegged into the upper parts of the rod and guard tube. The current and potential leads and the thermocouple wires were all brought out at the base, vacuum-tight seals being made by water-cooled wax-filled vessels.

In this set-up results were obtained for both thermal and electrical conductivities up to a temperature of about 800° C. It will be seen from figure 2 that over the temperature-range from 200° C. to 300° C., which was common to both the high-temperature and the low-temperature determinations, the values agree to within 2 or 3 per cent. At these temperatures the method employed for the elimination of heat-losses from the small rod would appear to be satisfactory. For tests at higher temperatures it was necessary to verify that the observed energy-input gave a true value for the flow of heat in the specimen. It was found impracticable to do this by measuring the temperature-gradient at the cold end of the rod, and a method resembling that used for the heat-resisting alloys $^{(1)}$ was eventually adopted, a short rod of the graphite being screwed into a rod of Armco iron of known conductivity $^{(6)}$. The details of the present set-up in the evacuated enclosure are shown in figure 1.

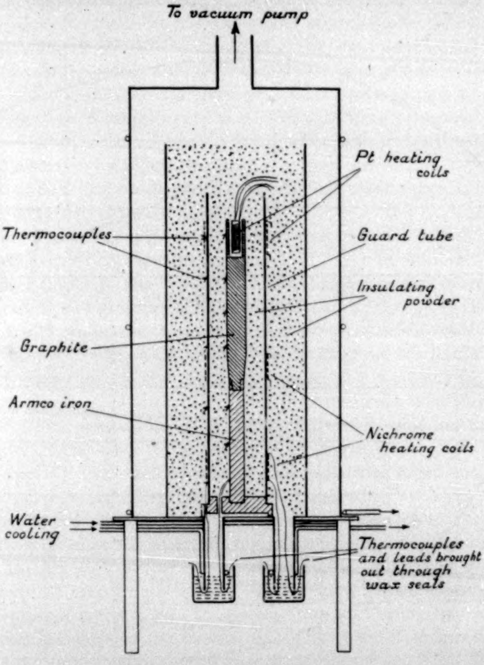

To vacuum pump
Pt heating coils
Thermocouples
Guard tube
Insulating powder
Graphite
Armco iron
Nichrome heating coils
Water cooling
Thermocouples and leads brought out through wax seals

Figure 1. Diagram of apparatus.

The values obtained for the thermal conductivity when this method was used are indicated in figure 2 and are seen to be in general agreement with those obtained in the previous experiment, except that they tend to lie on a somewhat lower curve at the higher temperatures. In drawing the final curve through the experimental points somewhat greater reliance has been placed on these latter values. With neither set-up was it found possible to extend the tests to temperatures much above 800° C., owing to failure of the upper heating coils.

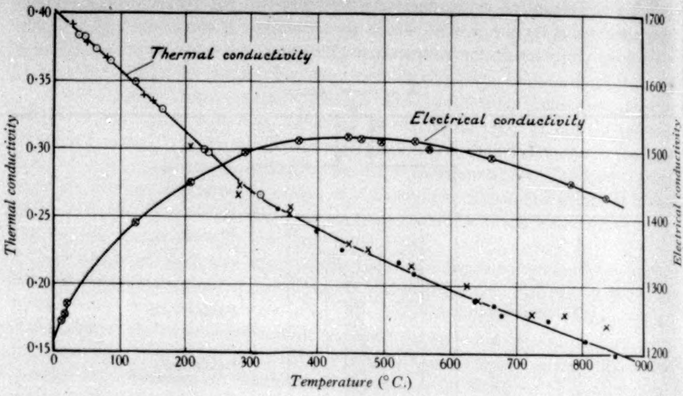


Figure 2. Variation of conductivities of Acheson graphite with temperature. Measured on thick rod, ⊙ ⊙ ⊙ ; on medium rod + + + ; on thin rod by first method × × × ; on thin rod by second method ....

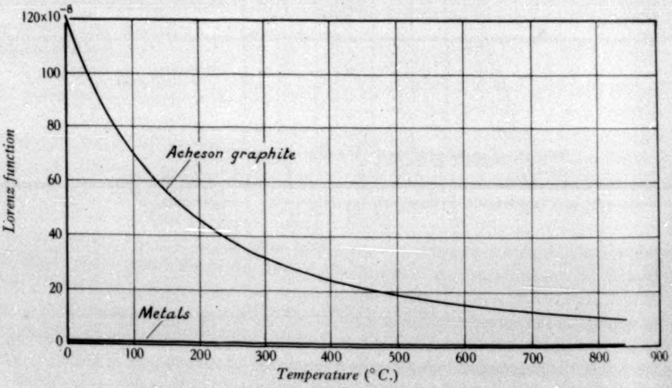


Figure 3. Variation of Lorenz function with temperature.

The curve showing the variation of electrical conductivity with temperature also is plotted in figure 2, whilst that for the Lorenz function, which has been derived from the smoothed values read from the thermal and electrical conductivity curves, is drawn in figure 3. For the purpose of comparison a curve giving the Lorenz function of normal metallic conductors has been included in the same figure.

§ 3. DISCUSSION OF RESULTS

Thermal and electrical conductivities. Graphite is produced when carbon is heated to extremely high temperatures. The physical properties of graphite differ considerably from those of carbon and vary to a lesser extent from sample to sample. The variation presumably depends on the completeness of the transformation, and thus on the temperature of firing, as well as on the purity of the material.

Published values for the thermal conductivity of graphite in the neighbourhood of atmospheric temperature have ranged from 0·037 to 0·85 cal. per cm. per sec. per degree, the corresponding values of the electrical conductivity being 52 and 3000 Ω^{-1}-cm^{-1}. The results for the more poorly conducting graphite were due to Barratt, the others to Koenigsberger and Weiss. Barratt's material, which was a lead extracted from a pencil, would seem to be an unusually poor graphite. Its electrical conductivity was less than that of amorphous carbon, which according to Störmer has an electrical conductivity of 114 Ω^{-1}-cm^{-1} and a thermal conductivity of 0·0048 unit at 13° C.

The present results fall between the above extreme values, and it should be realized that they apply to a particular sample of Acheson graphite. In a future paper the author hopes to deal with the thermal and electrical conductivities of a number of varieties of graphite.

It will be seen from figure 2 that whereas the thermal conductivity of Acheson graphite decreases with increase in temperature throughout the temperature-range covered by the experiments, the electrical conductivity increases to a maximum value at a temperature of about 450° C., and then decreases with further increase in temperature. This maximum value is 1·25 times the value indicated at 0° C. by extrapolation of the curve. The nature of the curve showing the variation of electrical conductivity with temperature agrees with that found for graphite by several other workers, including Noyes(7) and Nishiyama(8) but the temperature at which the maximum value occurs differs from sample to sample. The former used a rod of Acheson graphite for which he found a maximum value of 1·29 times the value at 0° C. to occur at a temperature of about 550° C. Nishiyama studied carbon filaments which had been graphitized to increasingly high amounts by heating to successively higher temperatures. It appears from his results that as the extent of graphitization is increased the maximum occurs at lower temperatures, and at the same time the ratio of its value to that at 0° C. decreases. An X-ray analysis of his specimens was undertaken by Nishiyama, and he considered that the electrical-conductivity results could be explained by the increased grain-size which accompanied increased graphitization.

Three determinations of the thermal conductivity of graphite have been made by other workers over the temperature-range covered by the present experiments. Hansen(9) determined the thermal conductivity of a 1-inch rod of Acheson graphite electrically heated at one end and water-cooled at the other. The rod was lagged, but no guards were used, so that the heat supplied exceeded that collected by the water-flow calorimeter. According to the values derived from the latter measurements, which are probably the more correct, the thermal conductivity decreased from 0·45 at 100° C. to 0·23 at 600° C. and lay from 25 to 15 per cent above that of the present sample of graphite. Hering(10) derived values for the thermal conductivity of graphite from observations on furnace electrodes. Mean values over large temperature-differences are obtained, and these values are probably less exact. They are, however, of the same order of magnitude and show a decrease from 0·34 at 245° C. to 0·29 at 510° C. Crary(11) has more recently carried out a determination on Acheson graphite, the source of heat being a flat coil sandwiched between two similar cylinders of graphite 4 in. in diameter. His values for the thermal conductivity range from 0·42 at 0° C. to 0·20 at 730° C. At these extreme temperatures the thermal conductivity is thus only 5 and 15 per cent greater than that of the present experiments. Crary's {conductivity, temperature} curve differs, however, in that it is convex with regard to the axis, and at 400° C. the value of the thermal conductivity is 0·34 compared with the 0·24 obtained in the present investigation. The explanation of this difference is not apparent, but it might be remarked that the method adopted by Crary for the prevention of lateral heat-loss appears to be unsatisfactory in that it assumes the material under test to have a constant thermal conductivity, whereas the conductivity of graphite decreases appreciably with increase in temperature.

The Lorenz function. It will be seen from figure 3 that the Lorenz function of Acheson graphite at 0° C. is some 200 times as great as that of most metals. With increase in temperature its value decreases rapidly, and graphite thus appears to fall in line with such metals as bismuth, nichrome, and F.H. stainless steel in that its Lorenz function approaches the electronic value when the temperature becomes sufficiently high.

A comparison of columns 4 and 5 in table 1 shows that the variation of the Lorenz function with temperature can be represented by the equation

$$L = K\sigma^{-1}T^{-1} = 0{\cdot}0294\,T^{-1{\cdot}8} \qquad \text{......(1)},$$

or

$$K\sigma^{-1}T^{0{\cdot}8} = 0{\cdot}0294 \qquad \text{......(2)},$$

where L is the Lorenz function, K the thermal conductivity in cal. per cm. per sec. per degree, σ the electrical conductivity (Ω^{-1}-cm^{-1}), and T the temperature (° K.).

Table 1. Comparison of values of L derived experimentally with those given by equation (1)

T	K	σ	L as $K\sigma^{-1}T^{-1}$	L as $0{\cdot}0294\,T^{-1{\cdot}8}$
273	0·402	1218	120·8 × 10^{-8}	121·1 × 10^{-8}
373	0·357	1369	70·0	69·1
473	0·312	1445	45·7	45·0
573	0·268	1497	31·3	31·9
673	0·240	1515	23·5	23·9
773	0·217	1517	18·5	18·6
873	0·197	1503	15·0	14·9
973	0·178	1476	12·4	12·3
1073	0·160	1444	10·3	10·3

Extrapolation indicates that at 3800° K., which approximates to the arc-temperature, the Lorenz function of graphite is about 1×10^{-8}, which is still somewhat greater than the theoretical value for metallic conductors.

This investigation has shown that although graphite has a thermal conductivity of the same order as that of many metals, it differs in that the Wiedemann-Franz-Lorenz law is not even approximately true. For the present sample of graphite this law can be replaced by the equation $K\sigma^{-1}T^{0\cdot8}$ = a constant, in which changes have been made in both the power to which the absolute temperature is raised and the constant value of the expression.

§ 4. ACKNOWLEDGEMENTS

The author desires to thank Dr G. W. C. Kaye, Superintendent of the Physics Department, for his continued interest in this investigation and for the provision of the necessary facilities. He is also indebted to Mr E. E. Smith, B.Sc. for assistance in the preparation of the specimens used in the earlier stages of the investigation and for taking some of the observations, and to Mr M. J. Hickman for rendering similar assistance in the final experiment at high temperatures.

REFERENCES

(1) Powell, R. W. *Proc. phys. Soc.* **48**, 381 (1936).
(2) Koenigsberger, J. and Weiss, J. *Ann. Phys.*, Lpz., **35**, 26 (1911).
(3) Barratt, T. *Proc. phys. Soc.* **26**, 347 (1914).
(4) Störmer, R. *Siemens K. Wiss. Verh.* **13**, 1, 30 (1934).
(5) *The Engineer*, **159**, 68 (1935).
(6) Powell, R. W. *Proc. phys. Soc.* **46**, 659 (1934).
(7) Noyes, B., Jr. *Phys. Rev.* **24**, 190 (1924).
(8) Nishiyama, Z. *Sci. Rep. Tôhoku Univ.* **21**, 171 (1932).
(9) Hansen, C. A. *Trans. Amer. Electrochem. Soc.* **16**, 350 (1909.)
(10) Hering, C. *Amer. Inst. Elect. Engrs*, **29**, 504 (1910).
(11) Crary, A. P. *Physics*, **4**, 332 (1933).

DISCUSSION

Prof. G. I. **Finch**. Structurally graphite consists of parallel hexagonal-network sheets of carbon atoms. The bindings between the carbon atoms in each sheet are homopolar and very strong but the bindings from sheet to sheet are very loose, of the free electron type, and this is the cause of the colour and good conductivity of graphite. The structure also accounts for the ease with which graphite can be cleaved into thin sheets, and in our laboratory we have succeeded in cleaving off sheets comprising as few as three or four hexagon layers. Such thin sheets are, as one might expect, almost as transparent as glass, and colourless. Owing to the loose binding between the sheets, the graphite structure can be expanded like a concertina by introducing oxygen or alkali metals which do not loosen the homopolar bindings but go in between the sheets. Thus we see that the properties of the graphite crystal in directions parallel and normal to the sheets are quite different, and we should expect to find great differences in the conductivity in a single crystal of graphite according to the direction in which the current flows. It would be of great interest to study the variation of conductivity with direction in a single crystal of graphite. The Natural History Museum possesses some very beautiful specimens containing single crystals measuring as much as 1 cm^3.

Miss M. D. WALLER. I should be interested to know how the conductivities of Acheson graphite vary at temperatures below 0° C., as I have found* maximal values of the vibration frequency or Young's modulus of specimens of Acheson graphite and carbon at about $-50°$ C.

Dr O. KANTOROWICZ. A high value of the Lorenz factor for a body like Acheson graphite does not necessarily indicate that the graphite crystals which constitute Acheson graphite show any anomaly at all. Acheson graphite is a kind of ceramic body and contains many pores, and also impurities, which must be suspected of being comparatively bad conductors for electricity and are most likely located on the grain boundaries. Consequently the electric current used to measure the resistance of the sample will flow from grain to grain through those rather restricted passages where one graphite crystal actually touches its neighbouring crystals, and the resistance to electricity of such an agglomerate is rather high. On the other hand the heat-flow is to a far lesser degree affected by the pores and impurities, both of which possess a certain conductivity for heat. The heat therefore flows along a path different from that of the electric current, and partly through other substances. Under these circumstances the quotient of electric and thermal conductivity is probably more a measure for the porosity and impurity of the particular sample than a characteristic of the constituent graphite crystals.

AUTHOR'S reply. I agree with Prof. Finch that it would be interesting to study the conductivities of a single crystal of graphite and appreciate the suggestion as to a possible source from which a suitable crystal might be obtained.

The experiments quoted by Miss Waller are of particular interest, as her observations on the elastic constants presumably indicate some change in the crystalline properties of graphite, and one inference from the high Lorenz function of this material is that a large proportion of the heat is conducted by crystalline rather than electronic processes. So far as I am aware the thermal conductivity of graphite has not been studied at temperatures below 0° C. and I hope to extend my measurements on graphite to lower temperatures.

The factors mentioned by Dr Kantorowicz may also play some part in explaining the high Lorenz function of graphite. X-ray analysis has not revealed any appreciable percentage of crystalline impurity in the specimen used in this work but amorphous carbon is probably present. It is hoped that the tests now in progress on other specimens of graphite will throw further light on the problem.

---

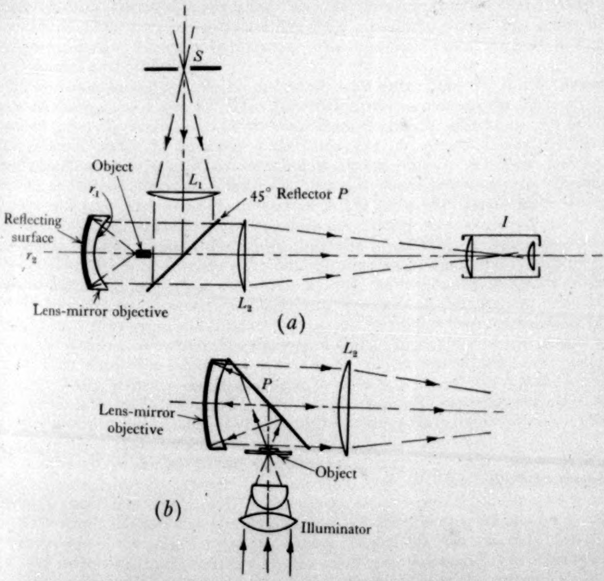
* *Proc. roy. Soc.* A, **157**, 388 (1936).

DEMONSTRATION

A MICROSCOPE FOR USE WITH ULTRAVIOLET LIGHT, EMPLOYING A REFLECTING OPTICAL SYSTEM OF APLANATIC PROPERTIES.

Demonstration given on 28 *May* 1937 *by* B. K. JOHNSON

Experiments have shown that transparent and opaque objects show marked differential absorption and reflection effects when observed with ultraviolet illumination under the microscope. By choosing appropriate wave-lengths, the desired amount of contrast in the image can be obtained; this act suggests a possible means of eliminating staining processes. In order to examine a specimen over a considerable range of ultraviolet wave-lengths it is necessary to have a number of quartz objectives, for it is not yet possible to achromatize the latter. This fact has led the author to design a simplified microscope objective in the form of a lens-mirror and


S
Object
L_1
45° Reflector P
r_1
Reflecting surface
r_2
I
Lens-mirror objective
L_2
(a)
L_2
P
Lens-mirror objective
Object
(b)
Illuminator

Reproduced by permission of the Journal of Scientific Instruments

The lens-mirror system as applied to the examination of (*a*) opaque objects, and (*b*) transparent objects.

one single lens. Up to numerical apertures of 0·55 such a system can be made free from spherical aberration and coma, whereas all surface-reflecting systems (such as the ellipsoid, the parabola, etc.) suffer from large amounts of coma immediately off the axis. The design of this optical system lends itself for use in the visible region of the spectrum provided that monochromatic light be used, and also in the infra-red. Its chief advantages over the orthodox quartz refracting objectives are (1) simplicity of manufacture and increased accuracy in the making of the surfaces; (2) increased contrast in the image due to reduction of number of air-quartz surfaces; (3) elimination of back-reflections when opaque objects are examined.

A full description of the instrument has been published.*

---

* *J. Sci. Instr.* **11**, 384 (1934).

REVIEWS

The March of Science, 1931–1935. By various Authors. Pp. viii + 215. (London: Pitman and Sons, 1937.) 3*s.* 6*d.*

After a long period during which specialization has been increasing, and has indeed been an explicitly announced goal, we seem to be entering on one with somewhat different characteristics. Specialization is of course not losing its importance, but it is now realized that the man who is only a specialist is not thereby superior to another who, in addition to his specialist knowledge, has also a background of wider culture. The changing viewpoint is to be found expressed in the frequent discussions of the examination system and the school curriculum, and is even reflected in popular literature. Wells unifies history, so that specialists in prehistory, archaeology, and the other branches are forced to meet each other and each to see his science against the background of the others. The same tendency is to be recognized in the recent publications of the masters of exposition, such as Andrade, J. A. Thomson and others.

When such a tendency is to be discerned, who better than the British Association should encourage and foster it? That Association was formed for the dissemination of knowledge, and the sections cover between them practically all science. In this book, which is issued under the authority of the Council, eminent practitioners of more than a dozen individual sciences give some account of the main lines of growth in their fields of work during the last five years. Naturally, their methods of treatment vary considerably, and they evidently differ widely as to the standard of knowledge which can be assumed in their readers, as well as in the degree to which they assume these readers desire to pursue the subject. Thus, whereas the physicist deems it desirable to offer an elementary explanation of how a probability wave can represent an electron, and to give us a rapid sketch of the growth of particle physics since 1895, the anthropologist speaks on his first page of the Icenian, Cromerian, Clactonian, Levalloisian, Mousterian, pre-Chellean, Acheulian and Micoquian cultures, and seems to suppose that they represent for us concepts as definite as those which they represent to him. Again, the zoologist gives a bibliography of more than 100 references, in four or five different languages.

On the whole, however, the authors seem to agree in a general way that the man in the street is an intelligent fellow who has some acquaintance with the achievements of science and a real desire to learn more—in short that he is the typical member (or rather, the ideal member) of the British Association.

The existence of this book, with its collection of surveys of recent advances in nearly all the sciences, naturally prompts us to ask the question, "What have been the greatest advances in science in that period?" The answer must depend a good deal on individual bias, but a survey of these chapters certainly seems to make out a good case for psychology as the recipient of the prize for rate of progress. Economics, it is true, may have changed more (and more often) than the others, but the result bears no evident signs of being a better science than its predecessors, whereas all the others do bear the outward signs of an approach to truth.

J. H. A.

Structure of Atomic Nuclei and Nuclear Transformations, by G. Gamov. Pp. xii + 270. (Humphrey Milford, Oxford University Press, 1937.) 17*s.* 6*d.* net.

Though formally a second edition of the author's well-known *Constitution of Atomic Nuclei*, the present volume is to all intents and purposes a new work. The astounding developments which have taken place in the last five years (including on the experimental side the discovery of the neutron and the production of artificial radioactivity, and on the theoretical side the fuller realization of the importance of interaction forces) have both revolutionized nuclear theory and widened its field. Very little of the old book survives in the present pages. It would be interesting, but fruitless, to speculate as to the contents of the next edition. Enough to say that in the present edition the argument moves freely and easily in a region so highly congested that the particles which inhabit it find it impossible to maintain even their identity.

Although the book deals with the theoretical rather than the experimental aspect of the subject, it is not unduly loaded with mathematical calculations, and no reader should be deterred from attempting it through lack of interest in the technique of wave mechanics. The author's main aim has been to discuss, in the clearest possible way, the principles employed in attempting to deduce the laws of physics within the nucleus, and the application of these laws to the problems of nuclear structure and nuclear behaviour. The interdependence of theory and experiment, the nature of the assumptions employed, and the occasional discordance between calculated and experimental results are displayed with clarity and candour. As a result, the book is not only an admirable survey of the present state of the subject, but a fascinating study of new knowledge in the making. The physicist who wishes for an adequate account of the philosophy underlying this new branch of physics will find his requirements well satisfied; and for those who may wish to pursue the mathematical calculations with greater rigour there are numerous references to original papers.

J. A. C.

The Physics of Electron Tubes, second edition, by L. R. KOLLER, Ph.D. Pp. xvii + 234. (International Series in Physics. London: McGraw Hill Publishing Co., Ltd.) 18*s.* 0*d.*

This book gives a very good survey of what takes place inside electronic devices in general. It does not discuss the details of circuits and methods of application of the various electronic tubes. The first four chapters deal with thermionic emission in principle, and cover thoriated tungsten cathodes, caesium on tungsten, caesium on oxygen on tungsten, and oxide-coated cathodes, and also a fair amount of general theory of thermionic emission. Secondary-emission phenomena and their applications are then dealt with, and afterwards special types of electron tubes are described. The omission of any reference to the X-ray tube here is rather surprising, and so is the brief nature of the paragraph on multielectrode tubes. Otherwise the field covered is fairly complete. There is an excellent chapter on the determination of the temperature of the electrodes in electronic devices.

The phenomena of the discharge in gases have been very ably worked into the general scheme of electronic tubes, and there follows a more practical chapter on grid-controlled arcs. There are then chapters on photoelectricity, photoconductivity, and the photovoltaic effect. In the latter two chapters the author has deviated from the title of electron tubes rather considerably, but they are written with the same clarity and conciseness as the rest of the book and therefore form a welcome addition to the text.

This book, which has now reached the second edition, has been brought very fully up to date, and is in touch with all the latest electronic developments. Sections have been added on electron optics, secondary emission multipliers, ignitrons, and positive-ion emission. It is an excellent book for the student of physics and electrical engineering, and will also be useful to the specialist engaged on research in other branches of physics in which these electron tubes find application.

J. A. D.

The Low-Voltage Cathode-Ray Tube, by G. PARR. Pp. x + 177, with 76 figures. (London: Chapman and Hall.) 10*s*. 6*d*. net.

This book should make a strong appeal to a large number of readers. It is sufficiently elementary for the more advanced students of physics and engineering and also sufficiently advanced to be of use to the research worker. The first chapter, entitled "Construction and operation", contains a general introduction to the principle of the cathode-ray tube. The second chapter deals with focusing and performance and is the only chapter in which some weakness makes itself felt. The treatment of electrostatic and electromagnetic focusing in this chapter is rather too scanty, and the distortion effects, as observed on the screen, are not dealt with as fully as one would have expected. The third chapter describes the formation of Lissajou's figures. This is a good feature because it revises a subject about which knowledge is too often taken for granted. The fourth chapter deals very fully with the essentials of the linear time base, and the next chapter goes on to other types of time base. The three remaining chapters deal with the various applications of cathode-ray tubes. In the first place to radio engineering, in the second place to general industrial problems, and finally to television. The chapter dealing with the industrial application is rather speculative, but the sections describing the uses of the cathode-ray tube in radio and television engineering are clear expositions of more well-known methods. The text is concise, but difficult points are explained with considerable care and the book is well illustrated throughout. The general quality of the publication is excellent.

J. A. D.

Atlas der Analysen-Linien der wichtigsten Elements, by Dr F. LÖWE. Pp. iv + 37, with 16 plates. (Dresden and Leipzig: Theodor Steinkopff, 1936.) RM. 10.

This is a second, and much changed, edition of the author's *Atlas der letzten Linien*, the new title being in accordance with Gerlach's nomenclature. To those engaged in spectrographic detection of the small quantities of elements in solutions, ores, alloys and other materials the work can be recommended as a saver of time and trouble. The author is the head of a section of the Zeiss works at Jena. In the first few pages are notes on apparatus and method (condensed spark between carbon electrodes on which a chloride solution has been evaporated) and on other atlases and tables (titles and references are listed). Then follow the 16 plates of selected regions of line spectra of 46 elements, and, printed on opposite pages, brief explanations and lists of wave-lengths. To the latter are added data for 11 elements not included in the plates. The book ends with a ten-page table of analysis lines between λ 1854 and λ 8944. A notable and commendable feature is the fewness of the lines included in this table and in the plates.

W. J.

Ions in Solution, by R. W. GURNEY. Pp. vi + 206. (Cambridge: The University Press, 1936.) 10*s*. 6*d*.

One of the characteristics that distinguish the best conjurers from those of the second rank is the fact that they send their audiences home impressed with the ease of the performance, and filled with the conviction that they have only to snap their own fingers in the air to find pennies in their hands. Dr Gurney shares these powers. Apparently provided only with the common sense necessary to depict qualitatively the form of the potential energy curve of an electron, ion or nucleus as the case may be in the presence of another particle or assemblage of particles, and furnished with a knowledge of what a Boltzmann factor is, he can draw forth the quantitative results of the Debye-Hückel theory so clearly as to persuade the reader that he could have done it himself without the help of these pioneers.

A very big claim is made in the preface, to the effect that the methods employed in the book can be expected to lead to an advance in ionic theory commensurate with that made in atomic theory by Bohr's methods. The reviewer is thus saved the trouble of deciding whether the book is or is not epoch-making—that is already decided for him. It does seem probable, however, that the claim can conscientiously be endorsed. It marks the epoch when attention is transferred from the salt in solution to the ions themselves, just as Bohr's theory completed what Ritz had commenced—the transfer of attention from spectral lines to energy levels.

This alteration in outlook leads (or will lead when the necessary quantitative data are available) to an easy understanding of the relation between ions *in vacuo*, ions in a crystal lattice and ions in solution. It permits of simple deductions relating to solubility, mutual precipitation, and electromotive forces and particularly the electrochemical series. It is very successful in dealing with optical absorption, and therefore with the colours of solutions, and must contain adequate information from which to calculate the electrical conductivity of an arbitrary solution at any degree of concentration. This last matter, however, is one to which little attention is devoted in the book under review.

The outstanding impression which the book leaves, is one of clarity, due to the facts that it is self-contained (there is not one reference in it to any scientific paper) and that the physical principles are kept so well to the fore. There are in it two suggestions that the author contemplates writing a companion volume containing a more detailed treatment, and it is to be hoped that in due course this will in fact appear.

J. H. A.

The Organic Chemistry of Nitrogen, by N. V. Sidgwick, F.R.S. New edition revised and rewritten by T. W. J. Taylor and W. Baker. Pp. xix + 590. (Oxford: Clarendon Press, and London: Humphrey Milford, 1937.) 25*s*. net.

The first edition of this book, published in 1910, has long been out of print and scarce, and the appearance of a second completely revised edition is welcome. The book deals with selected groups of organic compounds of nitrogen which are in themselves of considerable chemical and biochemical importance, and the treatment is very complete on the chemical side, from the point of view of both the theory and the experimental aspects. What differentiates the book from most treatises on organic chemistry is the unusually full discussion of relevant physical considerations, and at the present time, when so many organic compounds are the subject of study by physicists in various fields, the book is timely and of great interest and value. The eighteen chapters deal with the important groups of simpler organic compounds of nitrogen, and there are full references to the literature. The printing and paper are excellent and the moderate price is worthy of emphatic mention. This is a book of first-rate importance, and the new edition fully maintains the excellent features of the old. All the chemical considerations which must be known in dealing with any compounds from the point of view of physics or physical chemistry are explained, and the book is one which should be included among the works on chemistry in a physical library.

J. R. P.

THE CONDUCTION OF ELECTRICITY IN SOLIDS

Report of the
Conference held in Bristol from 13th to 16th July, 1937,
under the joint auspices of the Physical Society
and the University of Bristol

CONTENTS

PAGE

Introduction. By N. F. Mott v

PART I. CONDUCTION IN NON-METALS

R. W. Pohl. Electron conductivity and photochemical processes in alkali-halide crystals 3

R. W. Gurney and N. F. Mott. Trapped electrons in polar crystals . 32

Discussion 36

R. Hilsch. Alkali-halide phosphors containing heavy metals . . . 40

J. T. Randall. The effects of temperature on the intensity of fluorescence of some impurity solids 46

Discussion 57

J. H. de Boer and E. J. W. Verwey. Semi-conductors with partially and with completely filled $3d$-lattice bands 59

Discussion 72

PART II. CONDUCTION IN ALLOYS

G. Borelius. Resistance of alloys with disordered and ordered arrangement of atoms 77

W. L. Bragg, C. Sykes and A. J. Bradley. A study of the order-disorder transformation 96

C. H. Desch. Age-hardening alloys 103

Discussion 108

PART III. CONDUCTION IN THIN METALLIC FILMS

G. I. Finch. The structure of thin metallic films 113

E. T. S. Appleyard. Some factors influencing the resistance of thin metal films 118

A. Féry. A study of the electrical properties of thin films of platinum obtained by cathode sputtering in air and other gases (He, N_2, O_2 and H_2) 136

J. Bernamont. Fluctuations in the resistance of thin films 138

J. E. Lennard-Jones. The migration and aggregation of metal atoms on solid surfaces 140

Discussion 151

INTRODUCTION

By N. F. MOTT

Electricity may be carried in solids and liquids either by charged ions (electrolytic conduction) or by electrons. The papers in the present volume are concerned almost entirely with the conduction due to electrons. The first group of papers deals with conduction in insulators and semi-conductors, that is to say in solids in which there are normally at low temperatures no free electrons. They can only conduct if electrons are freed, either by irradiating the solid with light of a frequency which it can absorb, thus releasing electrons by a kind of internal photoelectric effect, or in the case of semi-conductors by keeping the solid at not too low a temperature, so that the thermal agitation of the atoms of the solid is able to free a few electrons.

The first paper is by R. W. Pohl, whose school in Göttingen has been for many years investigating photoconductivity in the alkali halides. These crystals do *not* show photoconductivity if they are illuminated in their own characteristic absorption band; in order to obtain photoconductivity one must first colour the crystal by the addition of some impurity or defect, which gives a new absorption band. The crystals used by Pohl are coloured by heating in the vapour of the alkali metal, which gives the well-known yellow colour of rock salt crystals or blue of KCl. The crystal shows photoconductivity if irradiated in the new absorption band so obtained. This band is known as the *F* band and the absorbing centres as *F* centres; their precise origin is at present uncertain, though hypotheses to explain it are advanced in the papers by Gurney and Mott and in the subsequent discussion.

An electron released from an *F* centre by the absorption of a quantum of radiation travels through the crystal only a certain distance before it is trapped, apparently in a less stable position called an *F′* centre. Thermal motion may release it, but it does not necessarily form another stable *F* centre until minutes or hours have elapsed. This suggests at once a mechanism for phosphorescence in crystal phosphors, on which we publish papers by R. Hilsch and by J. T. Randall. In the sulphide phosphors made by the addition of a heavy metal, it is possible that an electron is ejected from an impurity atom, forms an *F′* centre or something of the kind a long way off, and only re-radiates when it finds the parent atom again some time later. This hypothesis is supported by the temperature-dependence discussed by Randall, but cannot be applied to the alkali halides.

In semi-conductors free electrons are released, not by the absorption of light but by thermal agitation. In the theory given by Wilson in 1931 it is suggested that the electrons are released from impurities and defects; according to this theory the conductivity should be given by a law of the type $\sigma = Ae^{-E/kT}$. In the paper on semi-conductors by J. H. de Boer it is shown that experiment is in disagreement with theory in a number of ways. First, the parameter E depends often on the concentration of the impurity; and, secondly, there exists a number of semi-conductors which, according to the theory, ought not to be semi-conductors at all, but metallic conductors. These are ionic crystals with incomplete d shells, such as NiO. In the discussion of de Boer's paper, R. Peierls suggests that quite a drastic modification of the present electron theory of metals will be necessary if it is to include these substances.

The second group of papers deals with conduction in metals. Both on the experimental and on the theoretical side the study of conduction in metals is much further advanced than in insulators; so that, whereas in the latter case a host of problems remains to be investigated in connexion with the problem of conduction in the simplest substance, sodium chloride, in the case of metals we deal with problems of a more special nature.

G. Borelius gives an account of the work carried out by his school at the Technical College, Stockholm. This deals mostly with the magnetic and electrical properties of alloys and shows very clearly how the resistance is increased by the addition of any impurity which enters into solid solution, and also how the resistance is intimately related to the magnetism. Of especial interest is his account of alloys in which a superlattice can be formed, and his complete description from the point of view of thermodynamics of the transition between the ordered and disordered states.

W. L. Bragg describes his more recent attempt to obtain an atomic picture of the process, and the work carried out at the University of Manchester and at the laboratories of Metropolitan-Vickers by A. H. Bradley and C. Sykes. In this work again the conductivity and hence the mean free path are always found to be less in the disordered than in the ordered state.

C. H. Desch describes age-hardening alloys with especial reference to their resistance; the mechanism by which atoms in a supersaturated solid solution crystallize out is discussed.

The conduction of electricity in thin metallic films has been the object of a very large number of investigations. In an introductory paper G. I. Finch gives an account of the structure of such films as revealed by electron diffraction. E. T. S. Appleyard describes recent work by Lovell carried out under his direction in which apparently uniform layers of alkali metal are deposited on glass, and which, with a thickness of five or six atomic layers, have a resistance only about ten times greater than that of the bulk metal. The mechanism of conduction in so thin a film is discussed. In other metals (e.g. mercury) islands of metal seem to be formed, and the mechanism by which this can occur is outlined by J. E. Lennard-Jones. The different electrical properties that films of metal can have, according to their past history, is well brought out in the papers by A. Féry and J. Bernamont.

Finally a few words must be said about the account of the discussions published in this volume. This has been prepared by members of the staff of the Physics Department of the University of Bristol, who must take responsibility for the opinions expressed, since in the interests of speed of publication these summaries have not in all cases been submitted to the original speakers. No attempt has been made to include everything that was said; on the other hand, in certain cases remarks made in private discussion after the meetings have been included.

PART I

CONDUCTION IN NON-METALS

ELECTRON CONDUCTIVITY AND PHOTOCHEMICAL PROCESSES IN ALKALI-HALIDE CRYSTALS

BY R. W. POHL, Göttingen

§1. INTRODUCTION

THE fact that electrons can move about in the interior of highly insulating crystals was first definitely established in the case of the diamond(87). If a diamond crystal is placed in series with a battery of several hundred volts and a sensitive galvanometer, electron currents of the order of 10^{-9} A. may be observed upon illuminating the crystal with the light of a match. The number of crystals showing similar properties increased rapidly, but the observations continued to be generally of a qualitative nature. To be sure, it soon became evident that this phenomenon was related to photochemical processes, fluorescence and phosphorescence.

Quantitative measurements could be expected as soon as it became possible to work with artificially-produced crystals of well-defined chemical constitution. A series of preliminary experiments showed that this condition could be most simply fulfilled in crystals of the alkali halides. These can be produced with a high degree of chemical purity from fused salts. Single crystals of the size of an apple, or even having a content of a litre are relatively easily obtainable(9, 41). With the help of crystals so produced, the phenomena of electron conductivity and photochemical processes have been quite satisfactorily explained. The following report presents the most important results of the work, not a history of the individual problems. The investigations concerning fluorescence and phosphorescence processes are still in their initial stages, and will therefore not be included in this report, which is divided into the following four parts:

Part 1. The optical properties of the alkali-halide crystals in their pure state as well as when containing a stoichiometric excess of one of the components, i.e. either alkali metal or halogen (§§ 2–6).

Part 2. The motion of electrons released in the interior of these crystals through light, or more briefly: photoelectric currents in the crystals (§ 7).

Part 3. The motion of electrons thermally released, and the connexion between electron conductivity and ionic conductivity (§§ 8–9).

Part 4. Photochemical processes in the crystals (§§ 10–12).

Until 1926 these investigations were made jointly with B. Gudden (Gudden is now Professor of Physics at the University of Erlangen) and in later years with Dr Hilsch (now first assistant in my institute in Göttingen). Among numerous co-workers I should like to mention particularly: Z. Gyulai, E. Mollwo, A. Smakula, O. Stasiw, and recently G. Glaser, W. Lehfeldt, H. Pick and E. Rögener.

PART 1. THE OPTICAL PROPERTIES OF THE ALKALI-HALIDE CRYSTALS

§2. THE OPTICAL PROPERTIES OF PURE ALKALIDE CRYSTALS

The alkali-halide crystals, with their cubic lattice composed of positive and negative ions, probably represent the simplest type of solid body. They are perfectly transparent throughout a spectral range of almost six octaves and have a smooth dispersion curve, as illustrated in figure 1 for the case of LiF(16, 28, 41, 79).

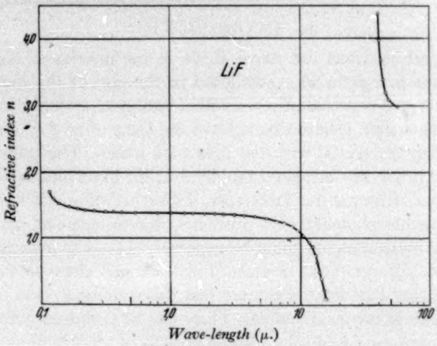


Figure 1.

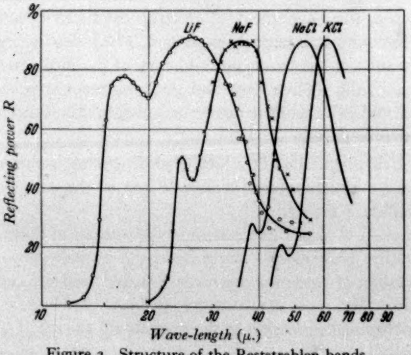
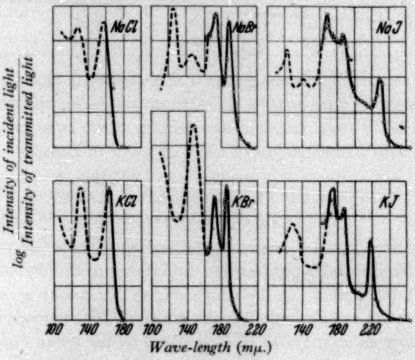


Figure 2. Structure of the Reststrahlen bands.

The rapid decrease of the index of refraction in the infra-red begins as soon as the region of residual rays (*Reststrahlen*), i.e. ionic vibrations, is reached. The structure of the residual ray bands is not as simple as supposed by their discoverer, Heinrich Rubens. Figure 2 gives typical curves for four salts(37, 79). The values of the absorption constants in the infra-red have been determined only for a limited range of wave-lengths. The measurements hitherto made do not suffice for a diagram.

In the ultra-violet, the state of affairs is quite different. There the absorption spectra, which cause the rapid increase of the index of refraction in the region of short waves, have been carefully measured(20, 23, 27). Figure 3 shows the absorption spectra of three Na salts and figure 4 of three K salts, which have recently been extended by the measurements of Schneider and O'Bryan(88). The similarity of spectra lying above one another is to be noticed.



Figures 3 and 4. Ultraviolet absorption of crystals.

The absorption constant K defined by the equation

$$J_d = J_0 e^{-Kd} \qquad \text{......(1),}$$

where J_0 is the intensity of the entering light, J_d the intensity of the transmitted light, and d the thickness of the specimen, has been measured for the first absorption bands of several salts in the form of thin films of thickness(49, 53) 2 to $10 \cdot 10^{-6}$ cm. These are given in table 1. In order to facilitate comparison with the absorption of light in metals, the values of the absorption coefficient $n\kappa$, defined by the equation

$$J_d = J_0 e^{-4\pi (n\kappa) d/\lambda_{\text{air}}} \qquad \text{......(2),}$$

have also been calculated, and are given in col. 4. The fifth column gives the molecular absorption constant β, defined by the equation

$$J_d = J_e . e^{-\beta N/F} \qquad \text{......(3).}$$

Here N is the number of molecules under the surface F and β represents the absorbing cross-section of the individual molecules for the incident photons.

These data are for crystals of the highest chemical purity obtainable. In experiments dealing with electronic conductivity, photochemical processes and luminescence phenomena, the starting material, if possible, should contain no more than one foreign molecule in 10^5 to 10^6 halide molecules. Greater concentrations of foreign molecules cause disturbances and the appearance of secondary effects(15, 45).

Table 1. Absorption in the first ultra-violet absorption band

Crystal	Wave-length of the band (mμ.)	Absorption constant K (cm.$^{-1}$ × 10^5)	Absorption coefficient $n\kappa$	Molecular absorption constant β (cm.^{2} × 10^{-17})
NaBr	192	10·0	1·53	5·5
KBr	189	8·8	1·33	6·3
RbBr	193	7·0	1·07	5·6
KJ	220	7·2	1·26	6·3
RbJ	223	7·0	1·24	6·9

Moreover, for a complete investigation it is necessary to know in addition to the optical properties of the pure crystals the changes which are introduced when small deviations occur in the stoichiometric composition of the crystals. It is possible to produce crystals with a small excess of alkali metal or of halogen.

§3. PRODUCTION OF ALKALI-HALIDE CRYSTALS WITH A STOICHIOMETRIC EXCESS OF ALKALI METAL

If an alkali-halide crystal is heated in the vapour of its cation metal, a stoichiometric excess of alkali metal is produced in the interior of the crystal, which imparts a bright colour to the crystal. In the simplest case this colour is caused by neutral alkali atoms which are loosely bound in the interior of the crystals in some manner or other. These foreign atoms shall be designated by the name *Farbzentren* (colour centres). The absorption spectrum has the form of a simple bell curve such as is shown in figure 5 for the five alkali-chloride crystals(18, 60).

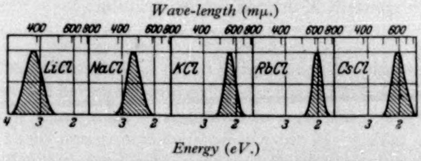


Figure 5. Absorption bands of the Farbzentren at 20° C.

The number of Farbzentren can be determined from the magnitude of the absorption constants and the half-width of the bands. The details of this calculation will be given in § 4.

The number of Farbzentren per cm.^{3} of the crystal is proportional to the number of metal atoms per cm.^{3} in the vapour surrounding the crystal(42). Figure 6 shows this fact for the case of KBr(80). In making these measurements, the vapour pressure of the metallic vapour and the temperature of the crystal could be varied independently of one another. The ratio

$$\alpha = \frac{\text{number of Farbzentren per cm.}^3}{\text{number of vapour atoms per cm.}^3}$$

is always greater than unity. Besides this, α decreases with increasing temperature of the crystal (see figure 7).

The binding of the Farbzentren may be described formally as a solution of alkali metals in the interior of the crystal. The law of mass-action may be applied and the

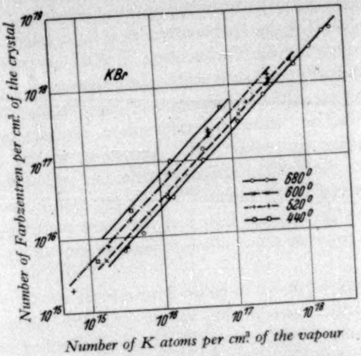


Figure 6. Solubility of K in a KBr crystal.

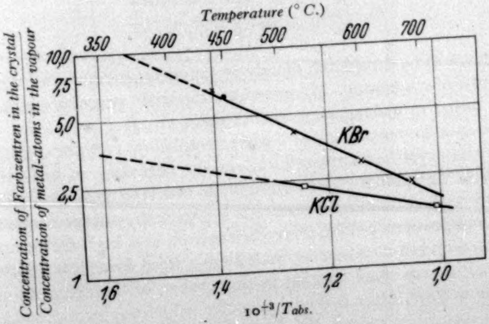


Figure 7.

constancy of the factor α would then mean that the process takes place without any change in the mol-number of molecules. This may be written as

$$K\text{ (in vapour)} \rightleftarrows K\text{ (in crystal)}.$$

According to this conception, the temperature dependence of the proportionality factor α may be considered as consequence of a positive binding energy W_F, according to the equation

$$\frac{d\,(\log \alpha)}{d\,(1/T)} = \frac{W_F}{k} \qquad \text{......(4).}$$

($k = 1{,}37 \cdot 10^{-23}$ watt-sec./° C.)

The binding energy W_F calculated by means of equation (4) from figure 6 gives the value $W_F = 0{\cdot}25$ eV. for the Farbzentren in KBr crystals, and from analogous measurements the value for the Farbzentren in KCl crystals is $W_F = 0{\cdot}10$ eV.(80). Measurements on the other salts are still in progress.

Just how this process of the introduction of extra atoms into the crystal lattice, here formally described as "solution" takes place, remains uncertain. It may be d? due to inner absorption processes(7, 8, 11). According to the experiments, as the temperature increases, the number of Farbzentren per cm.³ of the crystal approaches that of the atoms per cm.³ in the vapour(80).—As the melting-point of the crystal is passed, a new effect enters: Liquid KBr just above the melting-point is able to take up approximately 15 times as many alkali atoms per cm.³ as are present per cm.³ in the vapour(66).

Extrapolation of figure 7 down to room temperature 20° C., yields $\alpha_{\mathrm{KBr}} = 3{,}6 \cdot 10^4$ and $\alpha_{\mathrm{KCl}} = 9 \cdot 10^1$. Furthermore if the vapour-pressure curve for potassium is extrapolated to this same temperature, the resulting number of atoms per cm.³ is $7{,}5 \cdot 10^8$, and hence the equilibrium-concentration of Farbzentren in the crystal is

$$\left.\begin{aligned} c_{20^\circ} &= 3 \cdot 10^{13}\ \text{cm.}^{-3} \text{ for KBr} \\ c_{20^\circ} &= 7 \cdot 10^{10}\ \text{cm.}^{-3} \text{ for KCl} \end{aligned}\right\} \qquad \text{......(5).}$$

These figures are to be considered merely as rough approximations, which indicate simply the order of magnitude. Moreover, an important practical conclusion can be drawn from them: in making experiments ~~upon~~ electron conduction and photochemical processes concentrations of Farbzentren below 10^{15} per cm.³ can rarely be used. Otherwise crystals of great thickness are necessary in order to obtain a measurable light absorption.* Accordingly in order to have enough absorbing centres to work with at room temperature it is practically always necessary to use a quenched crystal previously filled with Farbzentren at a high temperature, whose higher concentration can be preserved in this way. In so doing it is unavoidable that a fraction, albeit a very small fraction in most cases, of the excess of alkali metal atoms combine to form larger colloidal particles, which are precipitated as foreign bodies(11). The absorption spectra of these colloids are very markedly affected by the particle size(32). In individual cases, where these colloids introduce secondary effects, they must be measured and considered. Fortunately, however, in most cases colloid formation can be so far suppressed as to be negligible.

---

* 10^{15} Farbzentren per cm.³ of KCl, for example, produce (at room temperature) an absorption constant of $0{\cdot}22$ cm.$^{-1}$; i.e. the light traversing the crystal must pass through a thickness of $4{\cdot}5$ cm. in order to be reduced to $1/e$ or 37 per cent of its original intensity.

§4. THE OPTICAL PROPERTIES OF THE FARBZENTREN

The absorption spectrum of the Farbzentren has a simple bell-shaped band, as was shown in figure 5. The form of this band is practically the same for all salts at the same temperature, as indicated in figure 8. In this figure(42) the curves obtained for the four salts have been reduced to the same abscissae by division by the proper frequency $\nu_0 = \nu_{\text{max.}}$. The curve drawn is that calculated on the basis of classical dispersion theory.

The form of the absorption spectra agrees well with the classical dispersion theory. The number N_0 of Farbzentren per unit volume(22), calculated on the basis of this theory, gives the equation

$$N_0 = 1{,}31 \cdot 10^{17} \frac{n_0}{(n_0^2+2)^2} . K_{\text{max.}} H \qquad \ldots\ldots(6),$$

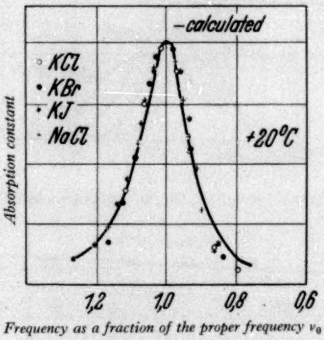


Figure 8.

where n_0 is the index of refraction of the crystal for the same wave-length of the band-maximum, $K_{\text{max.}}$ the absorption constant for the band-maximum in cm.$^{-1}$ according to equation (1), and H the half-width of the band in eV. This agrees very well with experiments. This equation may be written more simply

$$N_0 = A . K_{\text{max.}} . H \qquad \ldots\ldots(7).$$

The constant A, calculated on the basis of the theory for all halide crystals, has the average value of 10^{16}/eV. cm^2. Moreover, for KCl the constant A determined from an analytical chemical measurement(75) has the value $A = 1{,}31 \cdot 10^{16}$/eV. cm^2.*

The position and the form of the absorption spectra change decidedly with temperature(6, 10). As an example figure 9 shows measurements for KBr. A particular wave-length λ_0 is shown by a broken line. For each temperature this marks the point on the violet side of the absorption band at which the absorption-constant K has dropped to half the value of $K_{\max.}$. This wave-length has the same position for all

---

* If all the Farbzentren have been coagulated into small colloid particles, the absorption band changes in both shape and location. In spite of this fact, equation (7) may be used in making estimations, and at least gives values of the right order of magnitude(40).

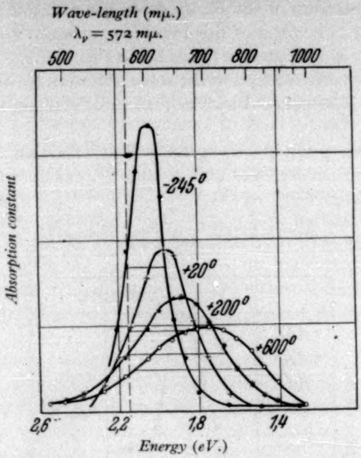


Figure 9. Absorption band of Farbzentren in KBr.

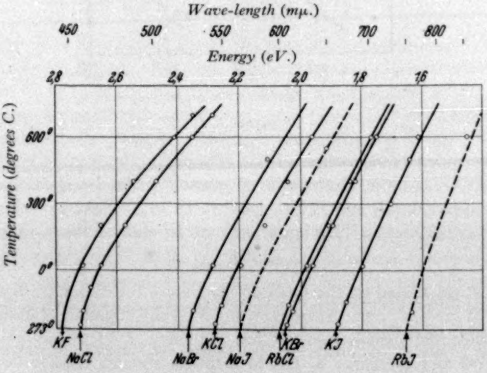


Figure 10. Absorption-band maxima of the Farbzentren.

temperatures (42). This may possibly be ascribed to a transition between two undisturbed energy levels of the crystal. Further, figure 10 shows the position of the band-maximum for nine different crystals as a function of the temperature. For any particular temperature there is a close connexion between the frequency ν_0 of the band-maximum and the lattice-constant d of the crystal under observation(30). At room temperature, the following relation is found to hold with close approximation

$$\nu_0 d^2 = 5 \cdot 10^{-5}\ \text{sec.}^{-1}\ \text{m.}^2 \qquad \text{......(8).}$$

§5. THE OPTICAL EXCITATION OF FARBZENTREN

By the process of light absorption the Farbzentren disappear and in their place there appear new centres, somewhat more loosely bound, which will be called *F′* centres. Their absorption spectrum extends further into the region of long wave-lengths, and the maximum also is shifted in this direction(4, 29). In favourable cases, the two maxima can be distinctly observed, as in figure 11. Curve *A* shows the absorption spectrum of the *F* centres before and curve *B* after excitation, i.e. after irradiation by light which was absorbed by the *F* centres. The excitation took place at − 100° C. On the contrary, both spectra, *A* as well as *B*, were made at − 235° C., in order to make the band as narrow as possible and thus to separate them distinctly. As a result of the excitation, the *F* band has been reduced by about two-thirds and in its place the shaded absorption band of the *F′* centres appears(86). These *F′* centres are stable only at low temperatures; they have only a limited life at higher temperatures(14), being changed back into *F* centres by thermal motion. At 250° these *F′* centres could not exist longer than one second in any crystal.

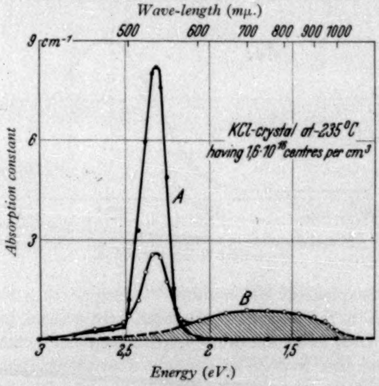


Figure 11.

Light absorption by *F′* centres, i.e. that of wave-length longer than 700 mμ. (as shown in figure 11) has the same effect as thermal motion. The transition $F \rightarrow F'$ is thus reversible(1). The quantum yield of the transformation $F \rightarrow F'$ has been measured repeatedly$^{(3, 22, 86)}$ but the investigations are not as yet completed. The ratio

$$\eta^* = \frac{\text{number of disappearing Farbzentren}}{\text{number of absorbed light quanta}}$$

is easily measured. More difficult, however, is the measurement of the ratio

$$\eta = \frac{\text{number of } F' \text{ centres formed}}{\text{number of absorbed light quanta}} \quad \ldots\ldots(9).$$

For temperatures down to $-130°$ C., $\eta = \eta^*$, but at still lower temperatures it has been possible to measure only η^*, and this has been found to have a value of approximately unity down to $-200°$ C. (Individual values between 0·4 and 1·6: the reason for this variation is still unknown.) Measurements of η at temperatures below $-150°$ C. have not as yet been successful. This is connected with another

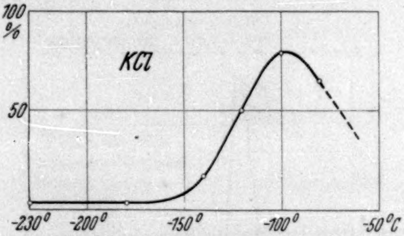


Figure 12. Ratio of decrease in number of Farbzentren due to excitation to number before excitation.

fact, also as yet unexplained: the number of disappearing Farbzentren is only initially proportional to the number of absorbed light quanta, but later approaches a saturation value. Only a fraction of the Farbzentren can be made to disappear by light absorption and this fraction is strongly dependent upon the temperature. Figure 12 shows an example of this, for the case of KCl. Principally noteworthy is the decrease in the direction of lower temperatures. The decrease towards higher temperatures is due simply to the experimental conditions. Here F' centres are produced by the disappearing Farbzentren, and the life of the F' centres is very short. By the time that the optical measurement of the number of centres has begun, a part of these F' centres has again disappeared. Further questions connected with figure 12 still need to be thoroughly investigated.

Note added in proof. Some new results are shown in figure 12 (*a*). The quantum yield for the $F \rightarrow F'$ transition begins at higher temperatures with the limiting value 2 and, as the temperature is lowered, falls much below 1; the dependence on temperature is much the same as for photochemical transitions (§ 12).

One light quantum can move only *one* electron; the latter can in the limiting case cause two Farbzentren to disappear and produce in their stead two F' centres.

The Farbzentren thus serve not only as sources of electrons, but their presence in the lattice also limits the range of the free electrons. An electron is ejected by a light quantum from a Farbzentrum and leaves in its place a positive alkali ion. The electron then diffuses in the electric field, and at the end of a finite range w is captured by a positive ion in the neighbourhood of another Farbzentrum. Thus it forms a new alkali atom. Both the neighbouring alkali atoms (which are in a region of ~~superfluous~~ excess negative charge) have an absorption spectrum somewhat different from that of two single Farbzentren, and appear optically in the form of two F' centres.

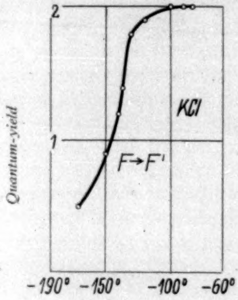
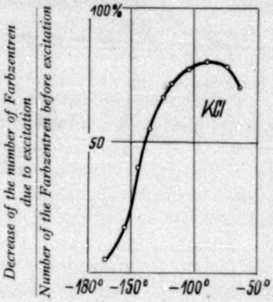


Figure 12 (*a*).



Temperature (° C.)

Figure 12 (*b*).

Figure 12 (*b*) shows newer measurements of the effect shown in figure 12.

The fact mentioned at the end of § 5 can be explained as follows: The quantum yield of the transition $F \to F'$ decreases with decreasing temperature, whilst the quantum yield of the transition $F' \to F$ retains its initial value. The equilibrium is thus displaced to the disadvantage of the F' centres.

§ 6. PRODUCTION AND OPTICAL PROPERTIES OF CRYSTALS WITH AN EXCESS OF HALOGEN

If an alkali-halide crystal is heated in the vapour of its halogen, a stoichiometric excess of halogen is formed in the interior of the crystal. This imparts a yellowish colour to the iodide and bromide crystals. Two absorption spectra(61, 83) for this case are shown in figure 13. The number of halogen atoms which have penetrated into the crystal can be determined from the maxima I and II* (the third maximum is due to a secondary effect, see below).

* Equation (8) is applied to both maxima, and the constant A is determined by an electrical method to be described later on. For iodine equation (6) may also be used.

(square not cube)

The number of halogen atoms per cm^2 of the crystal is proportional to the number of halogen molecules per cm^2 in the surrounding vapour(83). Figure 14 shows this for KBr as an example. In these experiments the temperature of the crystal and the vapour pressure could again be varied independently of one another. The relation

$$\gamma = \frac{\text{number of halogen atoms per cm}^3\text{ of the crystal}}{\text{number of halogen atoms per cm}^3\text{ of the vapour}}$$

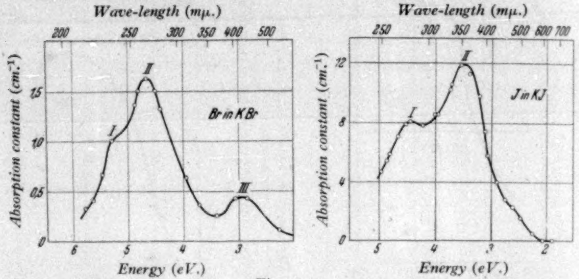


Figure 13.

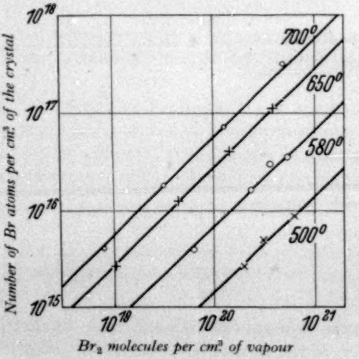


Figure 14. Solubility of Br in a KBr crystal.

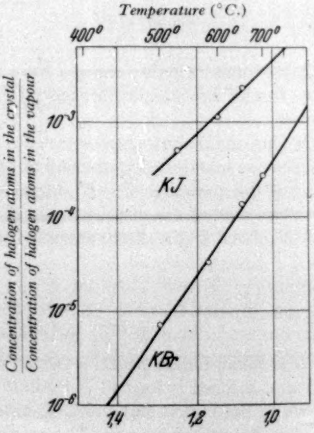


Figure 15.

never reaches unity. Furthermore, it decreases with decreasing temperature of the crystal (see figure 15). The process may here again be treated formally as a solution and a binding-energy of the halogen calculated, just as was done in the case of the excess alkali. This time the binding-energy is negative, being

$$w_{Br} = 1{\cdot}2 \text{ eV. for KBr}$$

$$w_{J} = 0{\cdot}8 \text{ eV. for KJ.}$$

This amount of energy must be given to the crystal in order to introduce an excess halogen atom (83), forming a molecule (see below).

The crystals, coloured at high temperatures, must be quickly quenched to room-temperature. Otherwise the excess halogen separates in individual clots as foreign bodies similar to the formation of colloidal metal particles. The maximum in the absorption spectrum of KBr, designated as III in figure 13, is due to such a precipitation, a slight amount of which is practically unavoidable.

The absorption spectra, i.e. the double bands I and II in figure 13, can thus by no means be ascribed to free halogen atoms. Rather similarly to the spectra of the Farbzentren, they are due to an adsorption compound of the type of KJ_3. The similarity between the absorption spectra of figure 13 and those obtained by de Boer and Custers (89) for the adsorption of halogen on vacuum-sublimated CaF_2 films speaks convincingly for this interpretation.

The mechanism of diffusion, by which the halogen penetrates into the crystal, is quite interesting. The discussion of this, as well as diffusion in the case of the formation of the Farbzentren will be dealt with in connexion with that of conduction (§§ 8 and 9).

PART 2. PHOTOELECTRIC CURRENTS IN THE CRYSTALS

§7. PHOTOELECTRIC PRIMARY CURRENTS IN CRYSTALS WITH EXCESS METAL ATOMS (FARBZENTREN)

The migration of the electrons ejected by the light and their replacement are designated as primary* photoelectric current. This replacement is necessary in order to neutralize the excess positive charge left on the atoms after the migration of electrons, and this can take place in two ways. In the first place, electrons which are later on ejected between the positively charged atoms and the cathode by thermal motion or by light ("electron-replacement-conductivity") may move in. Secondly, the neutralization may result due to electrolytic conductivity of the basic material (47). Unneutralized charges give rise to a polarization and decrease the electric field, often reducing the stationary photoelectric currents to values far below their initial values. This error can always be avoided by going over to the limiting case of sufficiently small light intensities. The fulfilment of this experimental condition is imperative.

* In contrast to photoelectric secondary current. This is lacking in the alkali-halide crystals, but in former years caused difficulties in the investigation of photoelectric properties in other crystals. The secondary currents are released in relay-fashion by the light, whereby an electron conductivity (already present without the presence of light) is increased for a long time by the action of the light. The numbers of electrons constituting the secondary current may exceed by a large factor those released by the light by a large factor. Compare the work of W. Lehfeldt (90).

The course of the primary photoelectric current as a function of time is strongly dependent upon the temperature(1, 70). Figure 16 shows this for the case of a NaCl crystal containing Farbzentren(72).

The total time of observation is divided into three intervals *A*, *B* and *C*. During the interval *A*, light is absorbed in the Farbzentren; *B* is an interval of darkness; and during the interval *C* the crystal is irradiated by light of long wave-length, which is absorbed practically solely by the *F′* centres.

At low temperatures, during the light-absorption in the Farbzentren there appears a practically constant current i_e, without any time lag(5). This is interpreted as follows(1, 48): the electrons ejected from the Farbzentren move towards the anode, and after traversing a mean range (*Schubweg*) *w* are brought to rest. This range is composed of many mean free paths and is usually much smaller than the distance *d* between the electrodes. Furthermore, exhaustive measurements have shown that it is proportional to the electric field strength *E*. The range is that component of the paths of the electrons in the direction of the anode in which their number is decreased to 1/*e* of the initial number, i.e. to 37 per cent. At the end of their range the electrons by combination with positive ions in the lattice form new centres with looser binding, which are *F′* centres.

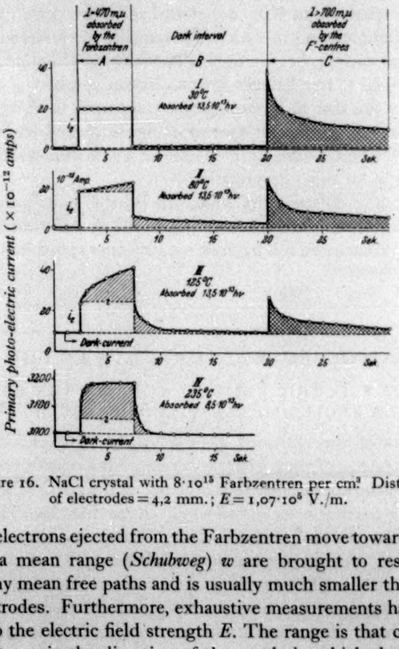


Figure 16. NaCl crystal with $8\cdot10^{15}$ Farbzentren per cm³ Distance of electrodes = 4,2 mm.; $E = 1{,}07\cdot10^{5}$ V./m.

At higher temperatures there appears during the period of illumination and after it during the dark period a decaying current whose course is shown by the shaded portion of the current-time curve. The interpretation of this is as follows:

The distance between the electron and the positively charged atoms is increased by thermal motion in the electric field. The electrons loosely bound in F' centres are dissociated thermally, proceed in the electric field, and are then again recaptured. This process can occur repeatedly, until the electron is again captured in an F' binding. Finally at low temperatures the thermal action can be either replaced (section I) or augmented (sections II and III) by a light-absorption in the F' centres as shown by the cross-hatched current-time areas of figure 16$^{(1, 12)}$.

In making quantitative observations, either the initial lagless primary photoelectric current i_e is measured, or, at higher temperatures, the total current-time area, including the non-shaded parts in figure 16. The relations which hold for this case are:

$$\eta \frac{w}{E} = \frac{i_e}{J_{\text{abs.}}} \frac{d}{E} P \qquad \text{......(10),}$$

and

$$\eta \frac{w}{E} = \frac{idt}{E_{\text{abs.}}} \frac{d}{E} P \qquad \text{......(11).}$$

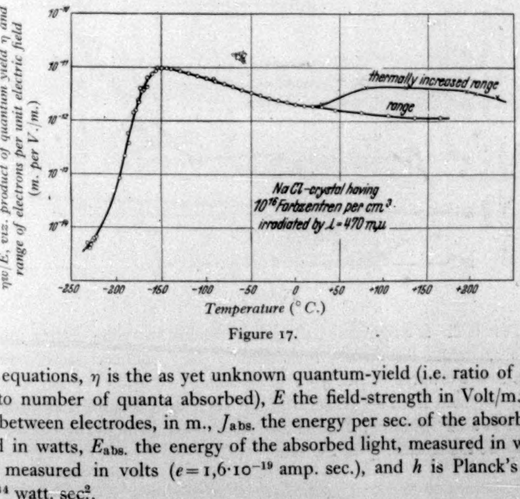


Figure 17.

In these equations, η is the as yet unknown quantum-yield (i.e. ratio of electrons set free to number of quanta absorbed), E the field-strength in Volt/m., d is the distance between electrodes, in m., $J_{\text{abs.}}$ the energy per sec. of the absorbed light, measured in watts, $E_{\text{abs.}}$ the energy of the absorbed light, measured in watt. sec., $P = h\nu/e$, measured in volts ($e = 1{,}6 \cdot 10^{-19}$ amp. sec.), and h is Planck's constant $6{,}55 \cdot 10^{-34}$ watt. sec^2.

The measurements were carried out at different temperatures, but without the introduction of long-wave-length light such as would be absorbed by the F' centres. This corresponds to the time intervals A and B in figure 16. Figure 17 shows the results for NaCl. For temperatures below 30° C. the course of the photoelectric current as a function of time corresponds to I of figure 16; for temperatures above 30° C., however, it corresponds to II–IV. Below 30° C. the electron ranges are calculated according to equation (10), and above 30° C. according to both equations (10) and (11) wherever possible, and at the highest temperatures by means of equation (11) alone. In this way one finds, for temperatures above 30° C., both the initial range (circles) and the additional thermally increased range (crosses). Both have been reduced to unit field-strength (1 V./m.) and multiplied with the as yet undetermined quantum-yield η.

Corresponding measurements have been made for NaBr, KCl, KBr, KJ, RbCl, RbBr and RbJ. In all cases essentially the same relations are found to hold. As a second example, figure 18 shows the measurements for KCl(85). The types of currents appearing at different temperatures have been schematically represented in the first row. Figure 18 shows a secondary effect not present in figure 17, namely a further increase in the range at the lowest temperatures.

A discussion of figures 17 and 18 should for the time being be limited to the first rise of the curve labelled "range", i.e. down to −150° C. for NaCl and to −130° C. for KCl. If a light quantum is absorbed in this temperature interval, not only a Farbzentrum disappears, but there is also produced an F' centre (§ 5). Therefore it is allowable to put $\eta = 1$ in equation (10) and (11), i.e. to assume an electron is liberated from a Farbzentrum for each light quantum absorbed, and is again fixed in an F' binding. In this case the curves through the circled observed points may be taken directly as the ratio

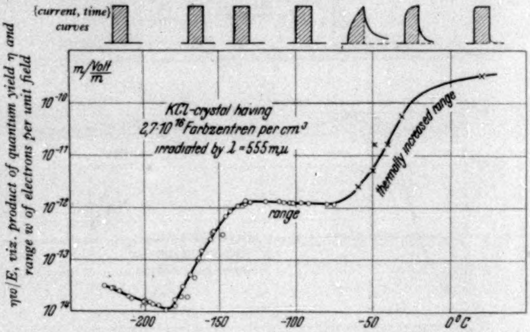


Figure 18.

$$\frac{w}{E} = \frac{\text{range of electrons}}{\text{field-strength}}.$$

The ratio w/E is proportional to a specific electric conductivity(77, 81). This increases initially with decreasing temperature not only for metals but also for isolating crystals as well. The absolute value of the temperature-coefficient is also of the same order of magnitude as for metals. Below the temperature designated, the value of η is as yet unknown. It is not known whether the sharp decrease of the measured value of $\eta\, w/E$ is due to a decrease of η or of w/E. A decrease of the mean range w would occur if some of the electrons liberated by light drop back into the metastable F' level of the same atom, instead of forming a new atom with a *distant* cation and taking a place in its F' level.

The new rise of $\eta\, w/E$ below −180° C. in KCl is certainly due to electrons which are liberated not from Farbzentren but from traces of colloids. Their small effect is not noticeable at high temperatures.

A further fact is important for the interpretation of this electron movement. The range of the electrons per unit field strength w/E is inversely proportional to the concentration of Farbzentren throughout a wide range of concentrations (figure 19). The measurements are for KCl at −100° C. and these have been made upon five different crystals, in order to show the magnitude of the individual variations(85).

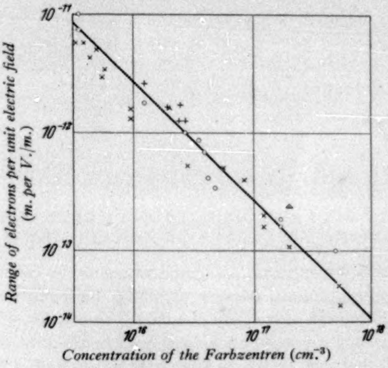


Figure 19. KCl at −100° C.

$1/w$ has the significance of an absorption-constant K_e as in equation (1), if J_e denotes the initial number of electrons and J_d their number after having moved a distance d towards the anode (this presupposes that the zig-zag path of the free electrons is large compared with the mean distance between Farbzentren). $K_e = 1/w$ is proportional to the concentration of Farbzentren, according to figure 19. Accordingly, the absorbing cross-section due to *one* Farbzentrum in the crystal may be calculated by means of equation (3) and at $E = 1$ V./m. this turns out to be $\beta_e = 4\cdot10^{-11}$ m.² for KCl, with numbers at the same order of magnitude for NaCl, KBr, RbCl, and RbBr.

Up to this point only the curves designated as "ranges" (circles in figures 17 and 18) have been considered. At higher temperatures the thermally increased ranges (denoted by crosses) have also been drawn. These are produced by a thermal diffusion of the F' centres. This diffusion is concluded only when all the electrons have returned to the stable Farbzentren binding. The paths traversed by the electrons up to this point in the case of KCl exceed the original range by up to 500-fold. At +20° the value of w/E is $5\cdot 10^{-10}$ V./m. At a field-strength of 10^6 V./m. the total path traversed by the electrons is thus 0·5 mm. In this case the electrons released by light in a crystal plate a few tenths of a mm. thick can be entirely withdrawn by the electric field and the primary photoelectric current then becomes saturated(17, 31).

Note added in proof. In favour of the hypotheses that the fall in $\eta w/E$ at low temperatures shown in figures 17 and 18 is due to a fall in η, we must add the fact that the quantum yield of the optical transition also decreases, and thus, apparently more than in proportion, the number of electrons which can move through the lattice decreases too. The drop in temperature inhibits the source of electrons, not the mechanism of conduction.

In favour of this explanation we may mention the observations made with KCl at low temperatures (figure 18) of a current due to electrons liberated from colloids by the ordinary surface photoelectric effect, which is known to be practically independent of temperature.

PART 3. MOTION OF ELECTRONS THERMALLY RELEASED

§ 8. THERMALLY RELEASED ELECTRON CURRENTS IN CRYSTALS HAVING AN EXCESS OF ALKALI METAL

The measurements shown in figures 17 and 18 cannot be carried out at temperatures above approximately 200°, because at higher temperatures not only the F' centres, but the Farbzentren as well are dissociated thermally. Consequently great numbers of free electrons are present even without illumination, in comparison with which the number that can be ejected by light is negligible.* For this reason Farbzentren cannot be used at high temperatures for the releasing of electrons by optical means. The thermal dissociation affects not only the Farbzentren, but also the lattice of the crystal, and thus the electrolytic conductivity of the basic material reaches a considerable value. At this stage, this electrolytic conductivity is able to neutralize the positive residual charges caused by the migration of great numbers of electrons.

At high temperatures these two facts cause the Farbzentren to migrate towards the anode as a swarm(33) (figure 20). This migration takes place with a definite rear wall. While the eye follows this, a current-measuring instrument shows the current-time curve(33) shown in figure 21.

Figure 20 corresponds formally to a series arrangement of two crystals having different electrical conductivities. In the part which is already clear, only ions migrate, whereas both ions and electrons migrate in the part still filled with Farbzentren. The number N of Farbzentren originally present in the crystal, which have migrated out of it due to the electric field can be calculated from the shaded current-time area, $\int idt$ of figure 21. Here

---

* Using monochromatic light, more than some 10^{14} quanta per sec. per cm^2 can hardly be introduced.

$$N = 2\frac{\int idt}{e} \qquad \ldots\ldots(12)$$

where $e = 1{,}6 \cdot 10^{-19}$ amp.sec. assuming that the electrolytic conductivity in the coloured part is no greater than in the clear part, in spite of the presence of the Farbzentren. Otherwise the factor 2 in equation (12) must be replaced by a smaller value, between 2 and 1 ⁽⁵¹⁾.

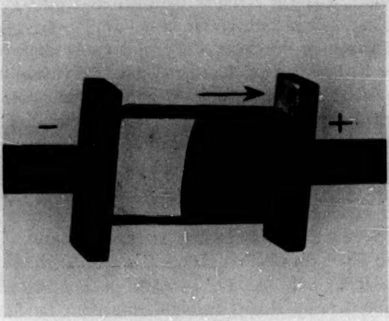


Figure 20.

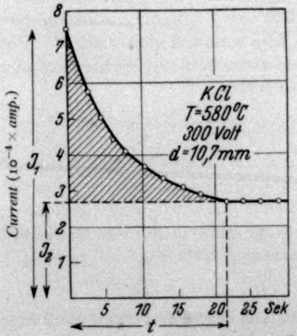


Figure 21. Electric current during the migration of Farbzentren.

The experiment represented in figure 20 can be varied. For example, electrons may be made to enter the crystal from a pointed cathode⁽³⁶⁾. A flat and previously anodically polarized cathode can also be used. In this way the whole crystal can be homogeneously filled with a Farbzentren swarm and an electron current i, constant with time, is obtained. The ionic current i_i due to the non-coloured crystal is superposed upon this. The relevant equation is

$$i = N_0 F e v_f \frac{P}{d}$$

where N_0 is the number of Farbzentren per cm.^{3}, F the cross-section of the crystal, $e = 1{,}6 \cdot 10^{-19}$ amp.sec., d is the distance between electrodes in m, P the applied voltage and v_f the mobility of Farbzentren in m.-sec.$^{-1}$/V.-m.$^{-1}$

The visible migration of the electron swarm is easily interpreted. The thermal dissociation of the Farbzentren produces invisible alkali-metal ions and electrons. The electrons are able to diffuse very quickly in the crystal lattice in traversing their free paths between the atoms of the lattice. If an electric field is applied to the crystal, the diffusion receives a preferential direction towards the anode. In this free condition each electron has only a limited life. This ends when the electron is captured by a positive ion and becomes fixed in the formation of a Farbzentrum. The electron then remains in this condition for some time, until it is again ejected by thermal motion, and the whole process starts over again. Only during these rest periods during which the electron is bound in the Farbzentrum, is the location of the electron rendered visible and in this way the path of the electrons towards the anode can be followed. Apparently, visible Farbzentren, i.e. neutral metal atoms, migrate; in reality, however, the migration is that of invisible electrons(67, 71).

The mobility of the Farbzentren, i.e. their speed of migration in unit electric field, can be measured in different ways. The simplest way is to observe a small, definitely bounded Farbzentren swarm in an otherwise clear crystal and to measure the velocity directly with a scale and stop-watch(44). Equation (12) may also be used(50) or measurements such as those represented in figure ~~20~~ 21 may be applied. The equation here applicable is(51)

$$v_f = \frac{1 + \frac{1}{2}(J_1 - J_2)/J_2}{TP} d^2 \qquad \text{......(13)}$$

(compare figure 10). Here T is the absolute temperature, P the applied voltage and d the distance between the electrodes.

The mobility measured in this way increases with the temperature of the crystal. Figure 22 shows this for nine salts. In all cases the mobility increases exponentially with temperature(44), according to the empirical formula

$$v_T = v_0 \, e^{-w/kT} \qquad \text{......(14)}$$

where $e = 1{,}37 \cdot 10^{-23}$ watt-sec./degree and w is a work-function.

Interpretation: with increasing temperature the thermal dissociation of the Farbzentren into ions and electrons increases, or, expressed in another way, the rest-periods of the electrons during their binding in the Farbzentren become shorter. In the limiting case of high temperatures these rest-periods disappear entirely and the mobility of the Farbzentren reaches its limiting value v_0. Several values(50) of v_0 will be found in table 2. These values are taken from the measurements represented in figure 22 and are not claimed to be exact. The limiting mobilities v_0 are of the same order of magnitude as that of the electrons in copper and in other metals of high conductivity.

Table 2.

	NaCl	NaBr	NaJ	KCl	KBr	KJ	RbCl	RbBr	RbJ
Limiting mobility v_0 m.-sec.$^{-1}$/V.-m.$^{-1}$	0·002	0·066	0·074	0·014	0·017	0·020	0·011	0·013	0·014
Thermal work function (eV.)	0·94	0·80	(0·76)	1·00	0·84	0·83	0·84	0·68	0·63

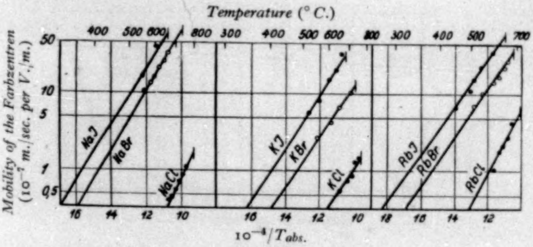


Figure 22. Mobility of Farbzentren.

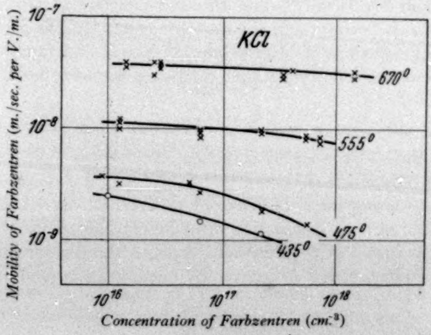


Figure 23.

In the experiments thus far discussed, small concentrations of Farbzentren have to be used. Otherwise the case might occur in which the electrolytic conductivity is not sufficient to neutralize the positive residual charges and thus the measured mobility is too small. Actually the concentration affects the true mobility, but its influence is very small, as figure 23 shows. It is only noticeable at low temperatures, the mobility of Farbzentren being practically constant at high temperatures(80) up to concentrations of $10^{18}/\text{cm}^3$.

By a proper choice of temperature-scales the curves of figure 23 for salts having the same cation may be made to coincide. In figure 24 the abscissae give the absolute temperature divided by a characteristic temperature for each salt, similar to that which may be derived from the specific heat as a function of the temperature, or in other ways. The ordinates, i.e. the mobilities of the Farbzentren, in contrast to figure 23, are plotted linearly, not logarithmically. From this it seems clear that the degree of dissociation of the Farbzentren, i.e. the exponential factor in equation (14), is determined practically by the thermal motion of the lattice.

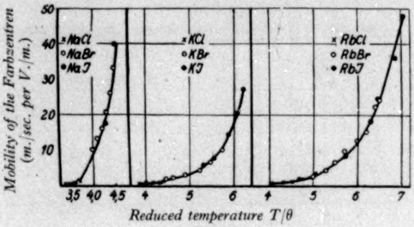


Figure 24.

If no electric field is applied to the crystal, the electrons which are thermally ejected diffuse in all directions(65). The diffusion-constant D can be measured and the same connexion between it and the mobility exists here as for these quantities in the case of ions in solutions(74). In the limiting case of high temperature or of very small concentrations the following simple relation is found to hold:

$$v_F = D\,\frac{e}{kT} \qquad \ldots\ldots(15),$$

where v is in $\text{m.-sec.}^{-1}/V.\text{-m.}^{-1}$ and D in $\text{m}^2/\text{sec.}$, $k = 1{,}37 \cdot 10^{-23}$ watt-sec./degree, and T and e are as in equation (14).

Beyond these limiting cases, the electrolytic conductivity of the basic material and the mechanism of ionic conduction must be considered(65, 56, 57).

The thermal diffusion of electrons also explains the phenomenon described in § 3, namely the production of Farbzentren by heating the crystal in the presence of the cation metal.*

§ 9. THERMALLY RELEASED ELECTRON CURRENTS IN CRYSTALS WITH EXCESS HALOGEN

The process discussed in § 8 may be concisely described as electron-excess conductivity. Neutral alkali atoms (Farbzentren) are changed over into positive ions, i.e. normal lattice elements, by giving off excess electrons. The counterpart of

* J. Eggert and W. Noddack(91) first introduced the idea of tracing back metallic diffusion to the diffusion of electrons, in order to explain the flocking together of silver atoms in AgBr crystals.

this, an electron-deficiency conductivity, can be observed in crystals having a stoichiometric excess of halogen atoms.* Here the visible neutral halogen is changed back into a negative ion, i.e. a normal lattice element, by taking up a lacking electron. This may take place in an electric field, according to the mechanism of electron-replacement (§ 7), if the thermal motion makes a thermal diffusion of electrons possible. Then a neutral halogen atom abstracts an electron from one of its neighbours between it and the cathode, and thereby itself becomes an invisible ion. At the same time it transforms its neighbour into a visible halogen atom. In this way the visible swarm of excess halogen wanders towards the cathode(61). The process is exactly the same as that illustrated in figure 20, with changed sign of the electrodes. Here again apparently a neutral halogen migrates in the electric field. Actually, however, electrons migrate according to the scheme of a replacement current.

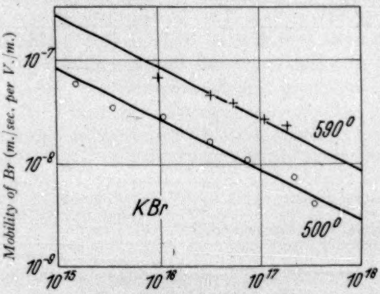


Figure 25.

Everything explained in § 8 may accordingly be applied to the electric measurements on crystals with excess halogen. Thus, for example, the current-time relation for the migration of a halogen swarm has the same form as in figure 21. The number of halogen atoms can be determined by equation (12). Furthermore the mobility of the halogen can be measured in exactly the same way as in the case of Farbzentren. In contrast with the Farbzentren, however, the halogen-mobility is greatly affected by the concentration(83), as shown by figure 25. Here also, however, the mobility increases with increasing temperature of the crystal, as figure 26 shows(83). The relation between the mobility v_T and the temperature may again be represented by the empirical equation (14). Table 3 contains several values for the limiting mobility v_0 and the work function w.

Thus there is an extensive analogy between electron-excess conductivity and electron-deficiency conductivity. However, there are noticeable quantitative differences. These pertain particularly to the thermal diffusion of halogen without application of an electric field. This difference was utilized in § 6 in the production

---

* The meaning of a stoichiometric excess of any electro~~n~~-negative lattice-element for thermally released electron currents was, to my knowledge, first recognized by B. Gudden(92). From this C. Wagner and W. Schottky have made deductions which are important in the problem of semiconductors.

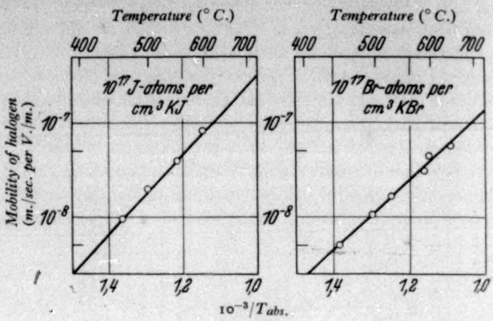


Figure 26.

Table 3.

	KBr	KJ
Limiting mobility v_0 (m.-sec.$^{-1}$/V.-m.$^{-1}$)	0,0007	0,005
Thermal work function (eV.)	0,7	0,8

of a stoichiometric halogen excess. This process takes place only partially by electron-diffusion. In the case of KBr under a halogen pressure of one atmosphere, for example, about 50 per cent of the diffusing molecules do so as uncharged bromine molecules (83).

PART 4. PHOTOCHEMICAL PROCESSES

§ 10. INTRODUCTION

The investigations of photochemical processes in solid bodies are carried out almost solely upon the silver salts, especially AgBr. This emphasis upon the silver salts is due to the extraordinary importance of photography. The majority of the investigations employ the conditions of exposure usual in photographic practice. Approximately 10^{14} light quanta per cm.^{3} are absorbed, and the number of molecules transformed, or the number of individual nuclei produced from them, is of the same order of magnitude. Under these conditions the action of the light is latent, since the silver-salt film of the photographic plates, etc. has a thickness of only a few μ. and consequently there are but 10^{10} transformed molecules under each cm.^{2} of surface (24, 38). In thicknesses as small as this, new molecules can first be optically observed when their concentration reaches 10^{18}/cm.^{3}, or when there are at least 10^{14} transformed molecules under each cm^2 of surface. For this reason, the aid of chemical development is necessary for investigations of such thin photographic films. A number of atoms of silver many thousands of times larger than the number of molecules originally transformed by the light must be deposited upon the primary reaction-products (or the nuclei resulting from them). If one wants to work without development, for example, with printing-out paper, at least 10^{18} quanta per cm^2 must be absorbed, a number far different from the normal-exposure condition.

Chemical development, although its practical use is very great, introduces serious difficulties into the investigations of photochemical questions. For this reason it seemed very interesting to be able to avoid the use of chemical development in the investigations of photochemical processes in solid bodies, and to make the elementary or latent action of the light directly observable. This problem was solved in a very simple manner for alkali-halide salts. The primary photochemical reaction-products in these are the Farbzentren. It is easy to work with clear crystals of 1 cm. thickness or more. It is sufficient, as in normal photographic exposure, to absorb approximately 10^{14} light quanta per cm^3. This results in 10^{14} Farbzentren under each cm^2 of surface, whereas in the thin photographic films the corresponding number was but 10^{10}. These 10^{14} Farbzentren are capable of investigation both optically and electrically. In this way it is possible to perform experiments upon the latent action of light, whose results may accordingly be applied to the technically important silver salts(26).

§ 11. PHOTOCHEMICALLY ACTIVE LIGHT-ABSORPTION

For the silver salts used in photography, the active spectral range coincides with the absorption band of AgBr extending into the visible. For many years the elementary process in photography has been interpreted as a removal of an electron from a halogen ion to a metal cation. The primary reaction-products were thought to be neutral silver atoms, and these were to be the preliminary step in the formation of the development-nuclei. In line with these photographic investigations, we at first used light, which was absorbed in the region of the first ultra-violet band of the crystal (figures 4 and 5) also in the case of alkali salts(25). This choice was favoured by the fact that the frequencies of the first band of all the salts can be satisfactorily calculated by assuming an electron transition from the anion to the cation and utilizing an empirical formula containing, aside from the lattice constants, only the ionizing potential of the metal and the two electron-affinities of the halogen(23, 35). For experimental reasons, only the long-wave end of the first absorption band could be used, for it was necessary to achieve a homogeneous penetration of photochemically active light through a crystal approximately 1 cm. thick. For the wave-length of the maximum of the first bands a thickness of only $0{\cdot}01\ \mu$. can be penetrated, because the absorption-constant here has a value of approximately 10^{-6} cm^{-1} (table 1). We may use only 10^{14} quanta per cm^3 in a volume 10^{-6} cm^3, giving 10^8 centres below an area of 1 cm^2, a much less favourable case than the 10^{10} per cm^2 in photographic plate.

This choice of photochemically active wave-length was, however, exceedingly unfavourable in another respect. The light-absorption in the long wave-length end of the first absorption band can, as stated above, be due to molecules of the lattice, which are thermally or otherwise disturbed and hence will respond to low frequencies. No less probable, however, is the absorption of light by foreign molecules(46), which can cause absorptions of the amount here utilized even when present only as impurities in a ratio of $1:10^6$. For this reason it was necessary to find a photochemically active light-absorption whose centres were definitely known. This has been possible.

The most favourable conditions exist in alkali-halide crystals containing small amounts of alkali hydride(78). Such mixed crystals may be produced in a number of ways. The best method is that of heating a crystal containing Farbzentren in an atmosphere of H_2. The H_2 diffuses rapidly into the crystal and changes the visible Farbzentren into invisible hydride molecules. At a pressure of 100 atmospheres this diffusion takes place with surprising speed, at a rate of approximately 1 mm./sec. (This is a diffusion of molecules, not protons(84)!) The alkali hydride, colourless in visible light, has a bell-shaped absorption band in the ultra-violet. Figure 27 shows the measurements for KH in KBr. These absorption bands were formerly designated as *U* bands of the salt, their origin then being unknown(39).

In a similar way crystals containing K_2O crystals can be produced, and their well-defined light-absorption utilized for photochemical purposes(55, 62). Certainly the number of usable additions is much greater(69, 76), but systematic investigations are still lacking.

§ 12. MEASUREMENTS OF THE PHOTOCHEMICAL YIELD BY OPTICAL AND ELECTRICAL MEANS

In gases, the photochemical dissociation of molecules is dependent not only upon the absorption of a light-quantum but also upon the thermal vibrational energy of the molecules as well. The same is true for the photochemical processes in the alkali salts, and also the optical dissociation of KH into invisible hydrogen and visible Farbzentren for example(52). If light is absorbed in the KH band (figure 27), this band disappears, and in its place the band of the Farbzentren appears. Figure 28 shows the yield of this photochemical reaction as a function of the temperature. This may be represented by the equation:

$$\eta_T = 1 - (1 - e^{-\epsilon/kT})^A \qquad \ldots\ldots(16),$$

where $\epsilon = 0{\cdot}85$ eV. and A has a value between 7 and 8(59, 82).

The number of Farbzentren formed was determined optically up to approximately 150° C. At higher temperatures this method fails, because the life of the Farbzentren becomes too short, due to their thermal transformation back into KH molecules(64). At higher temperatures, accordingly, an electrical method was applied for the measurement of the Farbzentren. The crystal is illuminated by light of known intensity, generally some 10^{-6} watt, amounting to some 10^{12} quanta per second, and the stationary photoelectric current is measured. If this is considerably smaller than the electrolytic dark current of the crystal, the current voltage curve shows a definite saturation (figure 29). The number of electrons migrating to the anode, and hence the number of Farbzentren formed, can be calculated from the saturation current(59). At the conclusion of the photochemical irradiation, the remainder of the Farbzentren can be observed as they move out of the crystal(46, 63, 73), just as is illustrated in figure 20.

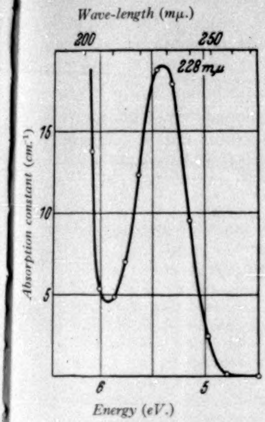


Figure 27. KH in KBr.

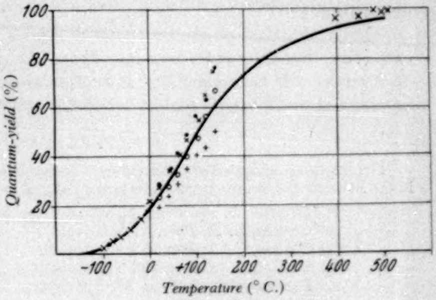


Figure 28.

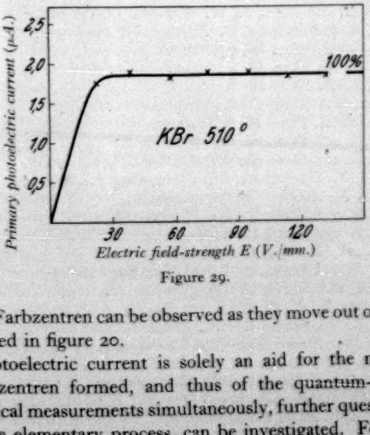


Figure 29.

Here the photoelectric current is solely an aid for the measurement of the number of Farbzentren formed, and thus of the quantum-yield. By utilizing electrical and optical measurements simultaneously, further questions, relating to the mechanism of the elementary process, can be investigated. For example, it turns out that the optical dissociation of the KH molecules and the formation of Farbzentren is not accompanied by a measurable current. The electron-transfer takes place only in molecular dimensions(76).

Electrical methods for the investigation of the photochemical elementary process may still be used even at low temperatures. If the number of Farbzentren formed in the available thickness of crystal does not suffice for the optical detection of these Farbzentren, the following method may be employed. Light is absorbed in the Farbzentren band, and the electrons can there be made as mobile as in the case discussed in § 7(29).

The investigation of photochemical processes in solid bodies is still in a very early stage. But a few of the facts found have been mentioned here. Still, the above illustrations will have served to show that these processes can be successfully investigated with physical means, i.e. optical and electrical observations, alone.

REFERENCES

The following list is that of publications of researches on *alkali-halide* crystals carried out in the Institute in Göttingen, which form the basis of this report.

(1) Gudden, B. and Pohl, R. W. *Z. Phys.* **31**, 651 (1925).
(2) Gyulai, Z. *Z. Phys.* **31**, 296 (1925).
(3) Gyulai, Z. *Z. Phys.* **32**, 103 (1925).
(4) Gyulai, Z. *Z. Phys.* **33**, 251 (1925).
(5) Flechsig, W. *Z. Phys.* **33**, 372 (1925).
(6) Gudden, B. and Pohl, R. W. *Z. Phys.* **34**, 249 (1925).
(7) Gyulai, Z. *Z. Phys.* **35**, 411 (1926).
(8) Pohl, R. W. *Naturwissenschaften*, **14**, 214 (1926).
(9) Kyropoulos, S. *Z. anorg. Chem.* **154**, 308 (Tammann-Festschr.) (1926).
(10) Flechsig, W. *Z. Phys.* **36**, 605 (1926).
(11) Gyulai, Z. *Z. Phys.* **37**, 889 (1926).
(12) Gudden, B. and Pohl, R. W. *Z. Phys.* **37**, 881 (1926).
(13) Hilsch, R. and Ottmer, R. *Z. Phys.* **39**, 644 (1926).
(14) Gyulai, Z. *Z. Phys.* **39**, 636 (1926).
(15) Hilsch, R. *Z. Phys.* **44**, 421 (1927).
(16) Gyulai, Z. *Z. Phys.* **46**, 80 (1927).
(17) Flechsig, W. *Z. Phys.* **46**, 788 (1928).
(18) Ottmer, R. *Z. Phys.* **46**, 798 (1928).
(19) Hilsch, R. and Pohl, R. W. *Z. Phys.* **57**, 145 (1929).
(20) Hilsch, R. and Pohl, R. W. *Z. Phys.* **57**, 145 (1929).
(21) Smakula, A. *Nachr. Ges. Wiss. Göttingen*, p. 110 (1929).
(22) Smakula, A. *Z. Phys.* **59**, 603 (1930).
(23) Hilsch, R. and Pohl, R. W. *Z. Phys.* **59**, 812 (1930).
(24) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, p. 176 (1930).
(25) Smakula, A. *Z. Phys.* **63**, 762 (1930).
(26) Hilsch, R. and Pohl, R. W. *Z. Phys.* **64**, 606 (1930).
(27) Fesefeldt, H. *Z. Phys.* **64**, 623 (1930).
(28) Gundelach, E. *Z. Phys.* **66**, 775 (1930).
(29) Hilsch, R. and Pohl, R. W. *Z. Phys.* **68**, 721 (1931).
(30) Mollwo, E. *Nachr. Ges. Wiss. Göttingen*, p. 97 (1931).
(31) Flechsig, W. *Phys. Z.* **32**, 843 (1931).
(32) Mollwo, E. *Nachr. Ges. Wiss. Göttingen*, p. 1 (1932).
(33) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, p. 261 (1932).
(34) Hecht, K. *Z. Phys.* **77**, 235 (1932).
(35) Hilsch, R. and Pohl, R. W. *Z. Phys.* **77**, 421 (1932).
(36) Pohl, R. W. *Naturwissenschaften*, **20**, 932 (1932).

(37) Korth, K. *Nachr. Ges. Wiss. Göttingen*, p. 576 (1932).
(38) Pohl, R. W. *Naturwissenschaften*, **21**, 261 (1933).
(39) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, p. 322 (1933).
(40) Miescher, E. *Nachr. Ges. Wiss. Göttingen*, p. 329 (1933).
(41) Korth, K. *Z. Phys.* **84**, 677 (1933).
(42) Mollwo, E. *Z. Phys.* **85**, 56 (1933).
(43) Lehfeldt, W. *Z. Phys.* **85**, 717 (1933).
(44) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, p. 387 (1933).
(45) Blau, M. *Nachr. Ges. Wiss. Göttingen*, p. 401 (1933).
(46) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, p. 406 (1933).
(47) Hilsch, R. and Pohl, R. W. *Z. Phys.* **82**, 78 (1933).
(48) Pohl, R. W. *Phys. Z.* **35**, 107 (1934).
(49) Bauer, G. *Ann. Phys.* Lpz., (5), **19**, 434 (1934).
(50) Smakula, A. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 55 (1934).
(51) Mollwo, E. and Roos, W. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 107 (1934).
(52) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 115 (1934).
(53) Kublitzky, A. *Ann. Phys.*, Lpz., (5), **20**, 794 (1934).
(54) Pohl, R. W. *Z. Metallk.* **26**, 217 (1934).
(55) von Lüpke, A. D. *Ann. Phys.*, Lpz., (5), **21**, 1 (1934).
(56) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 147 (1934).
(57) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 199 (1934).
(58) Mollwo, E. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 203 (1934).
(59) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 209 (1934).
(60) Pohl, R. W. *Kolloidzschr.* **71**, 257 (1934).
(61) Mollwo, E. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 215 (1934).
(62) Korth, K. *Nachr. Ges. Wiss. Göttingen*, N.F. **1**, 221 (1934).
(63) Pohl, R. W. *Z. tech. Phys.* **16**, 338 (1934).
(64) Hilsch, R. *Z. tech. Phys.* **16**, 341 (1934).
(65) Stasiw, O. *Z. tech. Phys.* **16**, 343 (1935).
(66) Mollwo, E. *Z. tech. Phys.* **16**, 346 (1935).
(67) Hilsch, R. *Z. angew. Chem.* **49**, 69 (1936).
(68) Pohl, R. W. *Umschau*, Heft 5 (1936).
(69) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 1 (1936).
(70) Thiele, W. *Ann. Phys.*, Lpz., (5), **25**, 561 (1936).
(71) Pohl, R. W. *Elektrotech. Zs.* **57**, 321 (1936).
(72) Glaser, G. and Lehfeldt, W. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 91 (1936).
(73) Glaser, G. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 109 (1936).
(74) Stasiw, O. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 131 (1936).
(75) Kleinschrod, F. G. *Ann. Phys.*, Lpz., (5), **27**, 97 (1936).
(76) Glaser, G. *Ann. Phys.*, Lpz., (5), **27**, 217 (1936).
(77) Naumann, A. *Ann. Phys.*, Lpz., (5), **27**, 233 (1936).
(78) Hilsch, R. and Pohl, R. W. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 139 (1936).
(79) Hohls, H. W. *Ann. Phys.*, Lpz., (5), **29**, 433 (1937).
(80) Rögener, H. *Ann. Phys.*, Lpz., (5), **29**, 386 (1937).
(81) Pohl, R. W. *Ann. Phys.*, Lpz., (5), **29**, 239 (1937).
(82) Schaitberger, G. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, 181 (1937).
(83) Mollwo, E. *Ann. Phys.*, Lpz., (5), **29**, 394 (1937).
(84) Hilsch, R. *Ann. Phys.*, Lpz., (5), **29**, 407 (1937).
(85) Glaser, G. *Nachr. Ges. Wiss. Göttingen*, N.F. **2**, in the press (1937).
(86) Pick, H. *Ann. Phys.*, Lpz., (5), in the press (1937).
(87) Gudden, B. and Pohl, R. W. *Z. Phys.* **3**, 123 (1920).
(88) Schneider, E. G. and O'Bryan, H. M. *Phys. Rev.* **51**, 293 (1937).
(89) de Boer, I. H. and Custers, I. F. H. *Z. f. phys. Chem.* B, **21**, 208, 1933.
(90) Lehfeldt, W. *Nachr. Ges. Wiss. Göttingen*, N.F., **1**, 199, 1935.
(91) Eggert, J. and Noddack, W. *Z. Elektrochem.* **32**, 496 (1926).
(92) Gudden, B. *Erlanger Berichte*, **62**, 289 (1930).

TRAPPED ELECTRONS IN POLAR CRYSTALS

By R. W. GURNEY and N. F. MOTT

Recently several attempts have been made to explain the nature and account for the properties of the *F* centres in terms of the atomic theory of polar lattices(1, 2, 3, 4), and it is a matter of dispute to what extent crystal imperfections and faults are essential for the understanding of this phenomenon. In this paper we shall attempt to show how an extra electron may be expected to behave in a crystal *without* crystal imperfections, if we accept the current theory of polar lattices, and shall then make some tentative suggestions about the connexion between our findings and the experimental material. The paper is based on an idea due originally to Landau(5) and developed further by Frenkel(6) and by ourselves. A very similar idea has been used by von Hippel(2).

If we imagine an extra electron brought from outside and placed on one of the metal ions of an alkali-halide crystal, then we should expect that electron to be free to move from one metal ion to the next through the crystal. Such an electron cannot be spoken of as belonging to any particular metal ion, and we speak of it as being in the conduction level of the crystal as a whole. In a crystal which shows photoconductivity the action of the light is to raise electrons from lower, bound, levels into the conduction level.

Now the dielectric constant of a polar crystal is due partly, as in non-polar materials, to the polarizability of the atoms or ions of which it is built up, and partly to the actual displacement of the positive and negative ions in opposite directions by the applied electric field. Owing to the large mass of the ions, they can only be displaced by alternating fields with frequency less than about 10^{12} sec.$^{-1}$ (the Reststrahlfrequenz).

We have used the methods of wave mechanics to investigate the motion of an electron in the conduction band and find that, as in a metal, an electron will not in general stay in the neighbourhood of any one ion for more than about 10^{-15} sec. The field of the electron itself, therefore, changes too rapidly to be effective in polarizing the medium. But suppose that "by accident" an electron remains on one positive ion for about 10^{-12} sec. Then the medium round about will have time to become polarized, the positive ions being displaced towards and the negative away from the electron as shown in figure 1 *a*. The electrostatic field vector E at a distance r from the electron will decrease (numerically) from $e/\kappa_0 r^2$ to $e/\kappa r^2$, where κ_0 ($\sim 2{\cdot}5$) denotes the dielectric constant due to the polarization of the ions only, and κ (~ 5) is the dielectric constant for static fields due to the polarization *and* to the displacement of the ions. The field due to the polarized medium is thus

$$\left(\frac{1}{\kappa}-\frac{1}{\kappa_0}\right)\frac{e}{r^2} \qquad \ldots\ldots(1).$$

This field will now push the electron back if it tries to escape; the potential energy of an electron in this field is

$$V(r) = -\left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right)\frac{e^2}{r} \qquad \ldots\ldots(2).$$

A "potential hole" is thus formed by the displaced medium, and in this potential hole the electron will have a series of stationary states, just like the stationary states in the field of a proton, for which $V(r) = -e^2/r$. We shall speak of an electron in the lowest of these states as a "trapped electron".

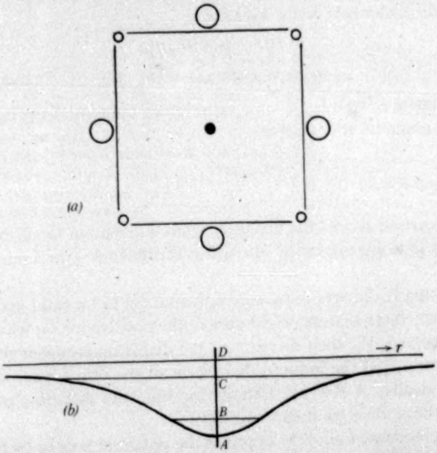


Figure 1. (*a*) Displaced ions round a trapped electron. (*b*) Potential energy of an electron in polarized crystal; the horizontal lines at B and C represent the energies of the normal and excited states. ● positive ion with electron; ○ positive ion; ◯ negative ion.

An electron trapped in this way can only move from one ion (*a*) to a neighbouring ion (*b*), if *at the same time* the surrounding ions move into new displaced positions about the ion (*b*). The frequency with which such a process takes place may be shown to be very small at room temperature(6), so that we may assume that our trapped electrons are immobile. At high temperatures, however, thermal vibrations may occasionally raise an electron from its trapped position into the conduction band.

Formulae (1) and (2) are valid only at large distances from the electron such that $r \gg a$, where a is the nearest distance between unlike ions. This is for two reasons: first, these formulae neglect the atomic structure of the crystal, and will be entirely incorrect when $r < a$; and secondly, an electron trapped in our "potential box" will have an orbit (wave function) of finite radius comparable with a, and some of the nearest ions will be acted on by a field due to *less* than one electronic charge. The potential energy of an electron in the field due to the displaced ions may be expected to appear as in figure 1 *b*. In this figure *B* and *C* represent normal and excited states.

We have estimated the depth of the potential hole *AD* in figure 1 *b* in a way which will be clearest if we neglect for the moment the polarizability of the ions and so set $\kappa_0 = 1$. Then at large distances the polarization of the medium is

$$P = \frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right)\frac{e}{r^2},$$

and thus the displacements of the ions are

$$x = \pm\frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right)\frac{a^3}{r^2} \qquad \text{......(3).}$$

If we were to assume formula (3) to be valid for *all* the ions of the lattice, we should obtain for the potential at the centre

$$-\frac{e^2}{4\pi}\left(1 - \frac{1}{\kappa}\right)\Sigma\frac{a^3}{r^4} = 1\cdot31\left(1 - \frac{1}{\kappa}\right)e^2,$$

where the summation Σ over the distances from a given ion to all the other ions of a simple cubic lattice was carried out using formulae due to Lennard-Jones and Ingham(7).

What we actually did was to assume equation (3) to be valid except for the six negative ions which are nearest neighbours to the positive ion on which the electron considered is located. We then determined the displacements x of these ions in the field of the electron and the induced dipoles of all the other ions, the latter being summed numerically. A few calculations for the ions distant $\sqrt{2}a$, $\sqrt{3}a$ and $2a$ showed this to be quite a good approximation.

By these methods we found the depth of the potential hole to be from 6 to 4 eV. for the fluorides and from 2·5 to 1·5 eV. for the other alkali halides. The displacement x of the ions which are nearest neighbours is of the order $\frac{1}{10}a$.

In a potential hole of the form shown in figure 1 *b*, an electron will have an infinite series of stationary states just as in a hydrogen atom. We therefore expect a strong-line absorption corresponding to a transition to the first *p* state, and possibly other weak lines. All lines will be broadened by the vibration of the ions. There will be also a weak continuous spectrum for higher frequencies.

The question now arises, can these trapped electrons be identified with the *F* centres? Both Smekal(3) and de Boer(1) have given quite different explanations. We see that the absorption to be expected is in the same part of the spectrum as the *F* band. We have, moreover, estimated the broadening to be expected as the temperature is raised and find it also in satisfactory agreement with experiment. The photoconductivity observed can be pictured in the following way: the electron is raised by the light to an excited state (*C* in figure 1 *b*), and the thermal vibrations are then sufficient to raise the electron into the conduction band. This will account for the very marked diminution in the current per absorbed quantum observed by Gläser and Lehfeldt(8) below −150° C.*; the thermal vibrations are *not* then sufficient to remove the electron.

Before, however, we can say with any confidence whether our trapped electrons are *F* centres, it will be necessary to discuss in the light of the model the various processes by which *F* centres may be formed, and what happens to the corresponding positive charge. We feel, however, that the theoretical grounds for believing in the existence of trapped electrons are strong, and that it will be surprising if they do not correspond to something in the observed phenomena.

REFERENCES

(1) de Boer, J. H. *Rec. Trav. chim. Pays-Bas*, **56**, 301 (1937).
(2) von Hippel, A. *Z. Phys.* **101**, 680 (1936).
(3) Smekal, A. *Z. Phys.* **101**, 661 (1936).
(4) Tarkakovsky. *Z. Phys.* **97**, 765 (1935).
(5) Landau. *Phys. Z. Sowjet.* **3**, 664 (1933).
(6) Frenkel. *Phys. Z. Sowjet.* **9**, 158 (1936).
(7) Lennard-Jones and Ingham. *Proc. roy. Soc.* A, **107**, 636 (1925).
(8) Gläser and Lehfeldt. *Nachr. Ges. Wiss. Göttingen*, **2**, 91 (1936).

---

* Cf. the paper in this volume by R. W. Pohl, figures 17 and 18, pp. 17, 18.

DISCUSSION OF THE PAPERS BY POHL, AND BY GURNEY AND MOTT

Reported by N. F. MOTT

THE discussion was opened by Dr de Boer, who remarked that although Prof. Pohl refused at this stage to advance any hypotheses as to the nature of the F centres (*Farbzentren*) until the experimental evidence should be sufficient to decide unequivocally between them, it was necessary for other people to do so, because of the great importance of this work of the Göttingen school for the understanding of other phenomena. He then proposed a number of alternative models for the F centres, which have already been published (reference 1 of the preceding paper). The following account describes the hypothesis, which, at the end of an afternoon's discussion, appeared the most probable.

It must first be stated that Landau's trapped electrons, described by Gurney and Mott, certainly do *not* correspond to the observed F centres. This follows from the fact (cf. Pohl's article, figure 6) that when a halide crystal is heated in the vapour of the alkali metal, the number of F centres formed is proportional to the pressure of the alkali vapour. If the alkali atom dissociated into a trapped electron and a positive ion (adsorbed perhaps at an internal crack), the number of F centres would be proportional to the square root of the ~~temperature~~. Whether Landau's trapped electrons correspond to anything in the observed phenomena must remain an open question.

alkali vapor pressure?

Any explanation based on cracks or defects of an *irregular* nature was ruled out, since Prof. Pohl stated that the spectrum of the F centres was always the same. This was not however definitely established to be the case for the F' centres.

The most probable hypothesis seems to be the following: in an alkali-halide crystal *in thermal equilibrium* at a temperature T one may suppose that at a certain number of positive lattice points, and at an equal number of negative lattice points, an ion is missing (cf. figure 1). The number of such vacant places will be proportional to a factor $e^{-\frac{1}{2}E/kT}$, where

$$E = E_1 + E_2 - E_3,$$

E_1, E_2 being the work required to remove a positive and negative ion respectively and E_3 the lattice energy per ion pair.*

It is now suggested that an F centre is an electron trapped in the neighbourhood of a point where a negative ion is missing. An F centre is thus as a whole electrically neutral.

---

* A preliminary calculation carried out in Bristol on the basis of the Born lattice theory with polarizable ions gives 1·4 eV. for $\frac{1}{2}E$ in NaCl.

If we neglect the finite radius of the orbit (wave function) of an electron, the energy of an electron located on a positive ion far from any hole will be

$$\frac{\alpha e^2}{r_0} - I \simeq +3 \text{ eV}.$$

where α is the Madelung constant (1·74), r_0 the interatomic distance, and I the ionization potential of the alkali atom. On one of the ions Q next to the missing negative ion the potential is

$$\frac{(\alpha - 1)\, e^2}{r_0} - I,$$

which is about 5 eV. lower, and at the lattice point of the missing ion the energy is $-\alpha e^2/r_0$, which is much lower still, so there is no doubt that an electron could be trapped in such a neighbourhood.*

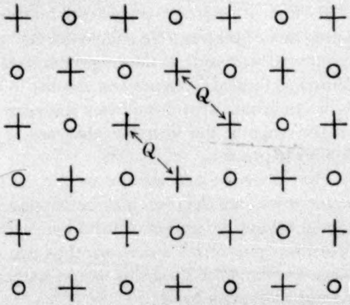


Figure 1. Alkali-halide crystal with one negative ion missing; the crosses represent positive and the circles negative ions. It is suggested that if an electron is trapped in the place left by the negative ion, an F centre is formed.

Dr Verwey suggested that the electron would be trapped on a particular one of the 6 ions Q, and described some recent experiments of his own on the dielectric loss for frequencies of about 200 metres in halide crystals with and without F centres. In the crystal with F centres the dielectric loss was some 50 times greater, although both crystals were insulators for steady fields. Dr Verwey suggested that this loss of energy was due to the electron jumping from one atom Q to another. In subsequent discussion with the present writer, however, it was agreed that the position of lowest energy is the central point, and that in any case an electron trapped in such a potential hole would have a non-degenerate wave function extending over the whole neighbourhood of the six points Q; so the explanation of Dr Verwey's experiments must be found in some other way.

The model given above of the F centres obviously accounts for the dependence of the concentration on the pressure of alkali vapour. Also, when F centres are introduced from a cathode into a hot crystal, halogen is ejected which, according to Prof. Pohl, can be detected by its smell. Further, the explanation of the drop in photoconductive current at low temperatures (Pohl, figure 17) given by Gurney and Mott can be applied to this model also. It also enables one to form a picture of the photochemical transformation of *U* centres into *F* centres. Assuming that a *U* centre is an H^- ion replacing a halogen negative ion in the lattice, the absorption of a quantum in the *U* band (Pohl, figure 27) will remove an electron on to a neighbouring positive ion, leaving behind a hydrogen atom. At sufficiently high temperatures the hydrogen atom will have time to diffuse away before the electron drops back to its normal state, so that an *F* centre is left behind. The necessity for the H atom to diffuse away will account for the fact that the quantum-yield drops low values at low temperatures (Pohl, figure 28).

---

* These energies, being calculated neglecting the polarizability of the ions, are probably much too large, but their relative magnitudes are correct.

Prof. Pohl mentioned the fact, not stated in his report, that in the optical production of *F′* centres from *F* centres, the absorption of *one* quantum destroys *two F* centres and forms *two F′* centres. He suggested that the electron released from an *F* centre is recaptured *most easily* in the neighbourhood of another *F* centre, and that the two *F* centres so formed influence one another in such a way that they give the *F′* absorption spectrum. This hypothesis accounts for the fact (Pohl, figure 19) that the mean range of the liberated electrons is proportional to the number of *F* centres already present.

On the hypothesis given above we may assume that, in the potential hole caused by the removal of a negative ion, *two* electrons may be trapped, just as two electrons may exist in the potential hole of the proton to form a negative ion H^-. What the absorption spectra reveal as a pair of *F′* centres are thus two electrons trapped in the same potential hole. On the other hand this would suggest that all *F′* centres should have just the same absorption band.

In conclusion, it must be emphasized that the correctness of the model given above is by no means proved. Prof. Pohl stated that he liked it the best of the various models suggested, but that further experimental work was required before it could definitely be accepted.

Dr W. F. Berg gave an account of experiments by himself and K. Mendelssohn on photographic sensitivity at low temperatures. According to present-day conceptions the photographic latent image consists of a small speck of silver, which has been formed by a primary photoelectric process and secondary processes which mainly consist of flocking together of silver particles and of getting rid of the bromine. Without going into the mechanism of these processes one can say that they imply the transport of matter through the crystal lattice. This transport should not be possible at sufficiently low temperatures, since the mobility drops with temperature as an exponential function. This was the reason for undertaking a preliminary determination of the photographic sensitivity down to 20° K. (liquid hydrogen). Measurements have already been done at 90° K., e.g. by F. Luft (*Phot. Korr.* **69**, 161–5 (1933)) and S. E. Sheppard, E. P. Wightman, and R. F. Quirk (*J. phys. Chem.* **38**, 817–31 (1934)). Defining sensitivity as the exposure necessary to give a density of 0·1 above fog it was found that (1) for a blue sensitive emulsion the sensitivity at 90° is 7 per cent, at 20° K. is 4 per cent of that at room temperature; (2) for a panchromatic emulsion at 20° the sensitivity is 0·4 per cent of the room temperature sensitivity for unfiltered tungsten light, 0·02 per cent for light filtered through a red No. 22 Wratten filter.

These results are in general agreement with the earlier papers as far as sensitivity at 90° is concerned. They have interest outside photography, which is possibly only a very sensitive means of studying the ionic conductivity in crystals. The sensitivity is surprisingly high in every case and can hardly be understood, if our conceptions are correct.

Prof. Pohl suggested that the actual transport of matter took place only after warming up.

Dr Berg also reported experiments on the print-out effect at 90° K. Solio paper gave a visible effect while still under liquid air, the sensitivity being reduced to about 10^{-5}. Slow Kodaline film gave no effect, the sensitivity being reduced to less than 10^{-6}.

ALKALI-HALIDE PHOSPHORS CONTAINING HEAVY METALS

BY R. HILSCH, Göttingen

§ 1. INTRODUCTION

THIS paper is an account of some of the work on the alkali-halide phosphors carried out in the Göttingen laboratory. The phenomena are simplest in phosphors activated by heavy metal halides(1, 2), and the discussion of these will form the main feature of this paper.

These phosphors can easily be prepared by adding to the molten alkali halides small concentrations of the heavy metal halides; the crystal phosphors can then be produced as single crystals and then the light absorption caused by the heavy metals can be measured easily. In most cases the absorption lies in the range of wave-lengths for which the pure crystal is transparent.

In contradistinction to most of the known phosphors, we are here dealing with the simplest lattices, only one kind of foreign atom being embedded within the body of the crystal.

§ 2. THE ABSORPTION SPECTRA OF THE ALKALI-HALIDE PHOSPHORS

It is often held that in these phosphors a real mixed crystal is formed, the heavy metal ions replacing the alkali ions in the lattice. The following discussion shows that this hypothesis must be accepted with reserve.

Figure 1 shows an example of a silver phosphor, the absorption spectrum of KI with 0·05 per cent AgI(3). A double band at 260 mμ. (at 20° C.) is observed to appear in the neighbourhood of the absorption edge of pure KI. At a temperature of 205° C., the band of longer wave-length alone is found. The behaviour with temperature of this transformation has been carefully investigated. With increasing temperature the intensity of the band at $\lambda = 265$ mμ. increases continuously. The transformation is complete at 148° C. This is a remarkable fact, for at the same temperature AgI possesses a point of transformation(4). In spite of the small concentration, the AgI structure is in some way still conserved within the KI crystal. The assumption that in the mixed crystals one silver ion replaces one alkali atom of the body crystal is thus ruled out.

The absorption bands of the phosphors so far produced, which contain the thallo-halides, are shown in figure 2(5). As well as the sharpness of the bands (in contrast to the diffuse bands of pure thallo-halides), it is striking that the halogen ions of the body crystal determine the situation of both the bands. This behaviour also does not agree with the assumption of a simple mixed crystal. It

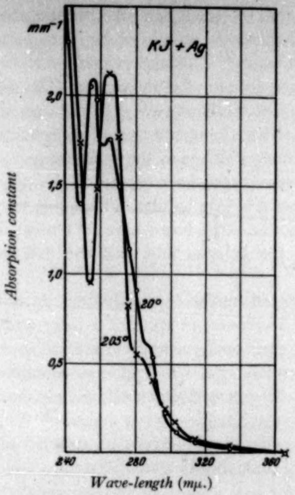


Figure 1. Absorption spectra of a KI phosphor activated by Ag above and below the transition point.

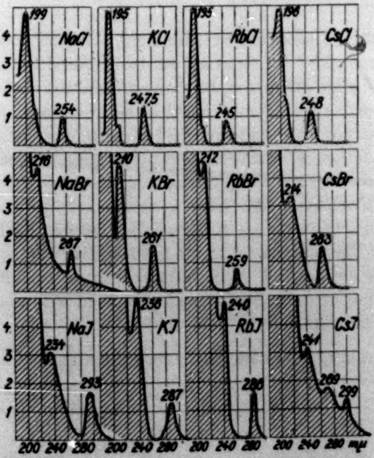


Figure 2. Absorption spectra of alkali-halide phosphors between 180 and 320mμ.

may also be mentioned that the small band in chloride phosphors lying at the foot of the short-wave band increases rapidly at high temperatures (over 500° C.) at the expense of the main band.(6) This also suggests a transformation of the lattice type of the centres responsible for the absorption. The distance between the two bands amounts in every case to about 1 eV. (In the case of chloride phosphors we take the band existing at high temperature.) This reminds one of the excitation energy of the thallium atom which is of the same value.

Similarly, measurements have been made of the absorption of alkali-halide phosphors with the addition of lead halides. The bands are found to be of the same sharpness. These will not be reproduced here. We must, however, stress the unimportant influence of the halogen ions and the determining influence of the alkali ions.

The phosphors activated by the copper halides do not show especially sharp regions of absorption. Moreover, in spite of a large addition of copper halides, only small amounts of copper can be actually dissolved in the atomic form. Several months later the absorption and with it the phosphorescent properties of the crystal are found to have disappeared almost completely, but they can be reproduced by a short period of heating(7, 8).

Thus, the formation of phosphorescent centres is only possible through the application of force, and then only to a small extent.

§ 3. THE MECHANISM OF THE ABSORPTION BANDS

After having noted these facts, the mechanism of absorption still remains to be explained.

Some experimental researches of Fromherz, Menschick and Kun-Hou-Lih are of great importance(9, 10, 11). Starting out from the already known absorption spectrum of alkali-halide phosphors, they investigated the absorption of the heavy metal halides in aqueous solutions. Besides the dissociated metal ions and the halogen ions, uncharged and positively charged molecules of the metal halides will be found in the solution, according to its concentration. The absorption bands of the aforesaid molecules have no similarity with those of the phosphors. When, however, we simultaneously add large quantities of the corresponding alkali halides (for example $H_2O + PbCl_2 + KCl$), we also find negatively charged complex ions (e.g. $PbCl_4$). The addition of alkali halides thus produces new absorption bands which may be ascribed to negatively charged complexes (MeX_n). The maxima of the bands of complex solutions, compared with those of crystal phosphors, are shown in table 1.

Table 1. Wave-lengths of absorption bands (mμ.)

	Crystal	Solution
$NaCl + AgCl$	210	216
$KCl + CuCl$	267	272
$KCl + PbCl_2$	273, 196	272, 195
$KCl + TlCl$	247, 196	242, —

The situation of the bands in solution as well as in the crystals is observed to be practically independent of the nature of the alkali chlorides. The bromides and iodides show the same behaviour.

From this Fromherz concluded that the active centres of the phosphors must have a structure simiiar to that of the saturated complexes. It must be supposed that within the crystal also there exists a rather isolated complex. This is easy to understand, when the great deformation produced by the heavy metal ion is taken into account. Thus we again approach the ideas put forward by Lenard and Schleede about the *Phosphoreszenzzentrum*.

§ 4. EMISSION BY ALKALI-HALIDE PHOSPHORS

We discuss only emission by thallium phosphors, which have been investigated thoroughly.

The emission consists of broad characteristic regions of emission with no remarkable structure. When illuminated with light of frequencies lying in the two absorption bands, the phosphors show fluorescence. On employing the radiation which is absorbed within the band at short wave-lengths, we also get phosphorescence up to 5 per cent. Fluorescence and phosphorescence give radiation with the same spectral distribution. One band, in particular, appears in the ultra-violet. The quantum yield, the decay of the after-glow and the spectral distribution of extinction have been closely investigated(12, 13, 14, 15). The results are not simpler than those drawn from sulphide phosphors. The interpretation of the mechanism of emission has not yet been given. It is only in the case of the rare earth phosphors that Tomaschek and his collaborators have succeeded in ascribing the emission to the various states of foreign atoms.

The question of energy transition seems to be the most important one. As has been pointed out in the investigations of Gudden and Pohl(16), a photoelectric conduction appears parallel to the excitation and the emission of the phosphorescence of sulphide phosphors. The electrons ejected by the irradiation are free to move. In contrast to this, the alkali-halide phosphors never show photoelectric conduction, when irradiated with any wave-length(17). We must conclude that in this case the electronic paths are very small and must be compared with the lattice distances. It is moreover certain that F centres will be produced by the accumulation of light-energy. We should suppose them to exist only in the vicinity of the *Zentrenkomplexe*.

In contrast to the absorption bands, the position of the emission bands depends upon the nature of the alkali ions of the body crystal. This is shown in table 2 for the thallium chloride phosphors.

Table 2. Maximum of the emission bands at 20° C. (mμ.)

NaCl	KCl	RbCl
288	300	315

Moreover, we find a considerable dependence upon temperature. The (TlX_n) complex must be considered if we are to interpret the emission bands. The excited states of these complex molecules, broadened by the energy of the lattice vibrations, are supposed to result in the unresolvable bands of the emission spectra. It is quite possible that these bands may be connected with the molecular spectra of thallo-halides investigated by Butkow(18). (Here spectra in the same region of wave-length appear as those emitted by thallium phosphors.) Hence the light absorption in the thallium complexes should cause excited states of thallium-halide complexes, which are similar to those of molecules in the gaseous state. (As has already been pointed out, the distance between the thallium absorption bands in all crystals amounts to about 1 eV., equal to the excitation energy of thallium atom.)

If the TlX_n complex is responsible not only for absorption but also for emission, the complex in solution in water should also show fluorescence. A short time ago I found that this was in fact the case. A strong bluish-violet emission can be excited in an aqueous solution of LiCl + TlCl by illuminating it with light of wave-length 242 mμ., the wave-length of the first absorption band of the complex (TlX_n). The bands of bromides and iodides move still farther towards longer wave-lengths in the visible region. These results seem quite reasonable, for the surroundings of the complex also in the crystal influence the emission spectra, as we see from table 2.

§ 5. PHOSPHORS WITH NO ADDITION OF HEAVY METAL

It has lately been found that at high temperatures gases are able to diffuse in the form of molecules within the pure alkali halide(19, 20). During these researches two further phosphors were produced(21). They were not activated by heavy metals, but by gaseous molecules, CO and O_2. Also in this case the absorption and emission must be ascribed to a complex. In the case of a crystal subject to a high pressure of O_2, ClO_4 might perhaps be the complex in question. The emission spectra are very remarkable. They consist of very sharp equidistant double bands. Their frequencies only depend to a small extent upon the body crystal used.

Until now it has not been possible to give a full explanation of these phenomena.

§ 6. SUMMARY

It is a remarkable fact that very complicated formations of molecules can be observed within the alkali halides in the form of single crystals. The luminescence processes which result from the construction of these complexes cannot as yet be interpreted. The exact process of absorption of light by the complex has also not been determined. Owing to their similarity with phenomena in aqueous solutions, however, the alkali halides have at least one advantage. Very definite complexes (MeX_n) may be shown to be responsible for the whole range of phenomena of light absorption and emission.

REFERENCES

(1) Hilsch, R. *Z. Phys.* **44**, 860 (1927).
(2) Smakula, A. *Z. Phys.* **45**, 1 (1927).
(3) Forró, M. *Z. Phys.* **58**, 613 (1929).
(4) Strock, L. W. *Z. phys. Chem.* B, **25**, 441 (1934).
(5) Hilsch, R. and Pohl, R. W. *Z. Phys.* **48**, 384 (1928).
(6) Forró, M. *Z. Phys.* **56**, 534 (1929).
(7) MacMahon, A. M. *Z. Phys.* **52**, 336 (1928).
(8) Forró, M. *Z. Phys.* **56**, 235 (1929).
(9) Fromherz, H. and Menschick, W. *Z. phys. Chem.* B, **3**, 1 (1929).
(10) Fromherz, H. and Kun-Hou-Lih. *Z. phys. Chem.* A, **153**, 321 (1929).
(11) Fromherz, H. *Z. Phys.* **68**, 233 (1931).
(12) Meyeren, von W. *Z. Phys.* **61**, 321 (1930).
(13) Bünger, W. *Z. Phys.* **66**, 311 (1930).
(14) Bünger, W. and Flechsig, W. *Z. Phys.* **67**, 42 (1931).
(15) Bünger, W. and Flechsig, W. *Z. Phys.* **69**, 637 (1931).
(16) Pohl, R. W. *Naturw.* **16**, 477 (1928).
(17) Hecht, K. Diss. Göttingen (1930).
(18) Butkow, K. *Z. Phys.* **58**, 232 (1929).
(19) Mollwo, E. *Ann. Phys.* **29**, 394 (1937).
(20) Hilsch, R. *Ann. Phys.* **29**, 407 (1937).
(21) Honrath, W. *Ann. Phys.* **29**, 421 (1937).

THE EFFECTS OF TEMPERATURE ON THE INTENSITY OF FLUORESCENCE OF SOME IMPURITY SOLIDS

By J. T. RANDALL

Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England

§ 1. INTRODUCTION

The present paper is largely an account of some preliminary measurements on the effects of temperature on the intensity of fluorescence of a number of impurity solids under photoexcitation.

During the last few years it has become clear that the properties of fluorescent solids requiring the presence of impurities are closely linked with those of semi-conductors. The zone theory of electronic energy bands in crystals has been successful in explaining, not only many features of the properties of metals, but, in principle at any rate, some of the features of semi-conductors.

It is not unreasonable to suppose that the same theory, or some modification, will ultimately be of great value in the study of fluorescence. At the present time, however, the difficulties of determining the energy zones in crystals with quantitative accuracy are extremely great, as may be seen from the recent work of Shockley(1) and Ewing and Seitz(2) on the alkali halides. Nevertheless, it remains true that no model of a fluorescent impurity solid other than that which depends on the division of the electronic energies into zones has been seriously proposed. It will be remembered that in the application of this model to certain types of semi-conductor by Wilson and Fowler, a notable feature was the temperature-dependence of the conductivity.

Very little work has as yet been carried out on the temperature-dependence of the intensity of fluorescence. In starting this work it was felt that the results might in due course help to throw some light on the mechanism of fluorescence in impurity solids, and possibly on the interchange of energy between "free" electrons and the lattice atoms. It is clear from the complex nature of the results that a great deal remains to be done.

As will be seen in more detail below, the greater number of powders examined consisted of zinc sulphides, or zinc-cadmium sulphides in solid-solution, each with various activating impurities. In addition, alumina and cadmium iodide were examined. It is necessary here to say a little about the zinc sulphide type of fluorescent material.

It is of course well known that the fluorescence effects observed with sulphides are a result of the presence within the solid of minute traces of impurity.* In this they differ from the uranyl salts, for example, where the seat of luminescence is in the co-ordination group of the uranyl ion, and the luminescence spectra are essentially molecular in type(6). It should also be noted that the sulphides, as distinct from the alkali halides considered by Hilsch(3), are photoconducting. The intensity of fluorescence of the sulphides is dependent, not only on the nature and amount of deliberate impurity, but on the complete exclusion of any other foreign material. In these compounds impurities to the extent of one or two parts in a million are frequently of vital importance whenever the details of the fluorescence spectrum have to be repeated with accuracy from specimen to specimen. In the silicates and phosphates, on the other hand, the optimum amount of impurity is frequently in the neighbourhood of from 0·1 to 1·0 per cent. From the point of view of the present experiments this means that one cannot assume that the only impurities present are those deliberately added at the outset of preparation; it is necessary to examine the final product spectroscopically in order to be reasonably sure of the total number of impurities. It was hoped at the start of this work to examine a number of zinc-cadmium sulphide solid-solutions, and also to compare the hexagonal and cubic varieties of zinc sulphide, all with the one impurity. The extreme ease with which sulphides of this group take up any extraneous impurity have made it impossible to carry out such an ideal programme, but the complexity of the results clearly suggests that further attempts in this direction will be worth while fundamentally.

Copious details for the preparation of fluorescent materials have been given from time to time(4), and it is only necessary to emphasize here one or two points of interest in connexion with the results which follow. The initial complex of pure matrix plus activating impurity has always to undergo a heat treatment in order that sensible fluorescence may subsequently be produced. It is also generally assumed that the activator during this treatment enters into solid-solution with the matrix. The work of Hilsch appears, however, to throw some doubt on this in the case of the alkali halides. The activating impurity is frequently added to the pure sulphide matrix in the form of a dilute solution to ensure adequate dispersion, and, theoretically, it should then only be necessary to heat the combination of the two to an appropriate temperature. While this procedure is successful with certain combinations of matrix and activator, others require the further addition of "fluxes". The avowed object of these is to promote crystal growth of the matrix and solid-solution of the main activator. Experiments show, however, that fluxes are frequently real impurities. Spectroscopic examination reveals their presence in the final material, and it is apparently impossible to remove them completely by means of washing processes.

* The work of Schleede(7) appears to show that strong blue fluorescence may be obtained from *pure* zinc sulphide, and the necessary condition for this is the presence of mixed crystals of wurtzite and blende. It is not improbable that the juxtaposition of the two types of crystal structure may be regarded theoretically as introducing at boundaries new levels which are effectively of the impurity type.

Before passing on to the experimental work a little must be said about the fluorescence spectra of impurity solids. Such spectra, where excited by ultraviolet, are characterized at room temperature by the presence of broad structureless bands, which may under certain special conditions be accompanied by very narrow bands with definite structure. The lowering of the temperature to that of liquid air, for example, results in a narrowing of the broad bands, but there appears to be no certain evidence that this is accompanied by development of structure within the bands.

The occurrence of very narrow bands, or even line systems, in the fluorescence spectra of impurity solids is usually due to the use of either chromium or one of the rare earths as activating impurity. The fluorescence spectra in cases of this kind are apparently partly made up of rather distorted line spectra of the ions of the activating impurities themselves. Presumably in this case the impurity levels lie just above the bottom of the conduction band. This aspect of the subject bears close resemblances to the work of Spedding⁽⁵⁾ on the absorption spectra of rare-earth salts.

In the more normal cases of fluorescence with structureless bands, the impurity levels will lie within the forbidden zone. On this view it is easy to see why different solids require different exciting wave-lengths. In order to excite electrons into the conduction band the exciting wave-length must have an *hν* value at least equal to that of the lowest energy values possible at the bottom of the conduction band. On this view the matrix lattice determines the exciting wave-length, and the impurity the fluorescence colour. In the well-known case of the ZnS/CdS sulphides with constant impurity the average wave-length of fluorescence increases as the cadmium content increases; it appears probable that this is due to the gradual lowering of the conduction band. Such ideas cannot at this stage be regarded as substantiated quantally; they merely serve to give a working picture of the process.

§ 2. SUBSTANCES EXAMINED AND EXPERIMENTAL PROCEDURE

The substances examined, together with the crystal lattices concerned and the impurities detected, are conveniently summarized in the following tables:

Table 1. Series of zinc sulphides

Powder and lattice details	Main impurities	Minor impurities*
(1) Cubic	Ag, Mg	Ba
(2) Hexagonal	Ag, Mg	Cd, Ba
(3) 75 % hexagonal 25 % cubic	Ag, Mg	Cu, Ba, Ni
(4) Cubic	Cu, Mg	Cd, Ba
(5) Hexagonal—slightly contracted lattice	Mn	Ba, Si

* Detected spectroscopically as traces.

Table 2. Series of zinc-cadmium sulphides

Powder and lattice details*	Main impurities	Minor impurities
13% CdS, 87% ZnS	Cu, Mg	Ag
16% CdS, 84% ZnS	Cu, Mg	Ba
24% CdS, 76% ZnS	Cu, Mg	Ag, Ba
29% CdS, 71% ZnS	Cu, Mg, Al	Ag, Ba
33% CdS, 67% ZnS	Cu, Mg	Ag, Ba

* The percentages refer to molecular proportions.

Table 3. Cadmium iodide and alumina

Powder and lattice details	Main impurities	Minor impurities
Cadmium iodide	Pb	Ag, Cu
Alumina—corundum type	Cr	—

The first column of each table describes the lattice and the constitution of the material, with the exception of table 2 where all the lattices are of the hexagonal type; the term "cadmium iodide" is by now sufficient both to describe the material and the lattice type. In the second column are given the main impurities, and it should be said that these have been identified not only as those which were deliberately added, but also spectroscopically by arcing the powders on graphite electrodes. In all cases where magnesium occurs it was added as flux material, and this also applies to the traces of barium. Any other impurities recorded in the case of the sulphides are accidental, and such as are likely to be picked up in any chemical laboratory by sulphides. It should be added that the compositions of the zinc-cadmium sulphides were determined by means of their X-ray patterns after the final heating process. This is an important point, as cadmium sulphide very readily evaporates from the solid-solution, and it appears that this is the only accurate means of determining the nature of the final product.

Although from general experimental acquaintance with this type of material one would consider it unlikely that variations of crystal size and lack of homogeneity in the powders are of greater importance than the impurities themselves, the X-ray apparatus revealed the following further information.

Table 4. Further details of the zinc-cadmium sulphide series of table 2

Percentage of cadmium sulphide	Details of homogeneity, crystal-size, etc. obtained from X-ray photographs
33	Crystal size about average for Zn/Cd sulphides. Outer diffraction lines fuzzy, indicating distortion or lack of homogeneity
29	Similar to 33% sample
24	Crystal size probably lower than above. Two distinct phases differing slightly in CdS content revealed by resolution of high angle diffraction line
16	Crystal size similar to 24%. Uniform composition
13	Crystal size similar to 24 and 16%. Two distinct phases, but very close together. Less difference than in 24%, and one phase weaker than the other

Where two distinct phases occur, the difference in CdS content is of the order of 1 per cent.

The fluorescence of the materials examined was excited by means of a high pressure mercury-vapour discharge lamp in conjunction with a Woods Glass filter. The excitation was therefore essentially that of the 3650 A. triplet. The fluorescence intensity was measured by means of a rectifier type of photoelectric cell in series with a galvanometer. The sensitivity of the cell varies a good deal according to the particular spectrum irradiating it, and no attempt has been made in this preliminary work to correct for this. The object of the experiments was mainly to obtain the general shape of the fluorescence-intensity temperature curves. The results are not therefore on an energy basis, and the fact that two powders may give rise to a particular deflection on the galvanometer at a given temperature has no special significance. As will be seen below, the room temperature deflection was usually chosen arbitrarily. At the present stage, also, the small colour changes which occur in the fluorescence spectra as the temperature is changed have been neglected.

With regard to the heating and cooling of the specimens, two pieces of apparatus were used, one for temperatures between 90° and 400° K., and the other from room temperatures to any high temperature desired. The measurements do not in fact extend much beyond 600° K. It was usually arranged for the two sets of readings on a particular specimen to overlap in temperature, in order to be sure of the continuity of the curves. For the higher temperatures the powders were dusted on to a miniature hot-plate fitted with thermocouple. The temperature of the surface of the powder was not exactly the same as that registered by the thermocouple, and the readings taken on a rising temperature scale differed slightly from those taken when the plate was cooling. In the curves reproduced later the means of these two sets of readings are plotted in each case. For the lower temperatures, down to that of liquid oxygen, a small thin quartz tube was used. The tube was fitted with a ground joint, and the cooling liquid poured into the tube, the powder being on the lower part of the outer surface. To insulate the powder from the atmosphere, and also to avoid condensation of moisture on the cooled powder surface, the cooling vessel is surrounded by an outer jacket, which is provided with means for evacuation. In this way it was found that uniform temperature over the whole of the powder surface could be maintained. In front of the photocell were placed a water filter and a Wratten *2a* gelatin filter to absorb any stray infra-red and ultra-violet. A set of readings was usually started by taking a "room temperature" deflection on the galvanometer with the ultra-violet source in a steady state. The distance of the source from the fluorescent specimen was then adjusted until the deflection was in a convenient region covered by the calibration curve of the photoelectric cell for different intensities of illumination. In the neighbourhood of room temperature water was normally used to aid the equalization of temperature over the surface of the inner tube. After removing the water, liquid air was poured into the inner tube and the equilibrium reading taken. The liquid air was then allowed to evaporate, and, just before this was achieved, a quantity of acetone at approximately the freezing point was poured in. This enabled another "fixed" point on the curve to be obtained, and provided a means of obtaining a comprehensive set of readings between approximately 180° K. and room temperature as the cooling liquid warmed up. The series was then completed by a few readings overlapping with the hot-plate temperature range, and for this either hot water or paraffin was employed.

§ 3. EXPERIMENTAL RESULTS

The general results may be summarized very briefly, although some of the details of the various curves will require further discussion. It appears, for all the substances examined, that there is a critical temperature above which the fluorescence intensity always falls fairly rapidly and uniformly. At still higher temperatures the rate of decrease of intensity with temperature decreases. Below what has been called the critical temperature for convenience, a variety of things may happen. In certain cases the intensity may remain sensibly constant as the temperature is reduced; in others there may be a continuous fall; in the zinc-cadmium sulphides there are usually two maxima, and it is the higher temperature maximum that has been associated with a "critical" value of the temperature.

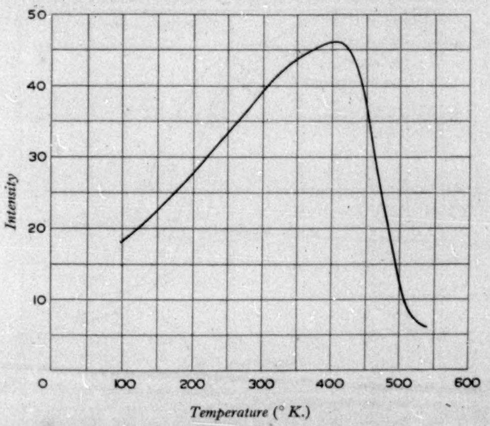


Figure 1. Zinc sulphide hexagonal. Impurities Mn, Mg, (Ba), (Si).

It is convenient to consider first of all the case of hexagonal zinc sulphide with manganese as the main impurity; this is the substance numbered (5) in table 1. For this the intensity variation with temperature appears to be of a fairly simple nature (figure 1). Starting at 100° K. the intensity rises almost linearly with temperature to a maximum value at about 400° K., followed by a sharper linear drop in intensity. Finally at about 500° K. the curve flattens out. It should be noted that this particular powder has a slightly contracted lattice, due no doubt to the presence of manganese sulphide in solid-solution.

Turning now to the curves of figure 2, where the results for the remainder of the "pure" zinc sulphides are recorded, we see that they differ a good deal from those for the manganese-activated powder of figure 1. With the exception possibly of (3) the slopes of the high temperature portion of the curves is rather less, and the low temperature behaviour is considerably different. In three cases, those of powders (3), (4) and (2), there is a distinct small hump at low temperatures, while powder 1 has a minimum at about 180° K. It must be admitted that the complication of the multiple impurities makes it a difficult matter to be certain of the interpretation to be given, but one or two points may be made. First of all comparing powders (2) and (4), it is noticed that in spite of the difference in structure, and the difference in one of the main impurities, these curves are very similar in shape. We are led to assume that in such similar crystal structures, the differences are not of importance, or, if they are, they have been conveniently smudged out by the difference in impurity. If the differences in structure are unimportant, then copper and silver appear to give very similar results. Assuming this, and turning to (1) on the same figure, the minimum in the low temperature part of the curve appears to be associated with the absence of cadmium.

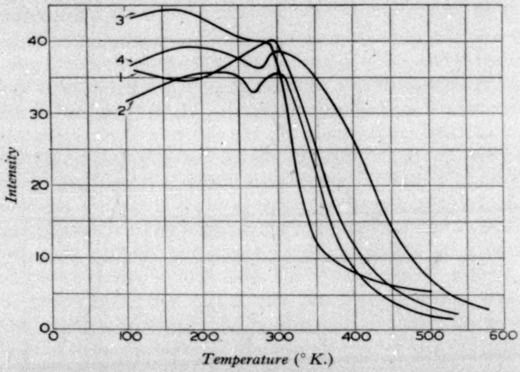


Figure 2. Effect of temperature on fluorescence of cubic and hexagonal ZnS with various impurities. (1) cubic ZnS, Ag, Mg, (Ba); (2) hexagonal ZnS, Ag, Mg, (Cd), (Ba); (3) hexagonal + cubic ZnS, Ag, Mg, (Cu), (Ba), (Ni); (4) cubic ZnS, Cu, Mg, (Cd), (Ba).

In figure 3 are reproduced the curves for the solid-solutions of zinc and cadmium sulphides, and with the exception of curve (*e*), representing the 29 per cent cadmium solid-solution, the curves show strong similarities to curves (2), (4) and (3) of figure 2. It is to be noticed that Cu is a common impurity for all the specimens of this series. Although silver is absent only from (*c*) with 16 per cent CdS, its absence makes no general difference to the shape of the curve, which is essentially similar to curve (*a*), which is curve (4) of figure 2 reproduced here for comparison. A further point of interest is that the low temperature peak becomes more pronounced as the proportion of cadmium is increased. In curve (*e*) this peak quite dwarfs the room temperature peak. In the case of the 29 per cent CdS of (*e*) it is interesting to note that the single curve obtained has no obvious peak and appears to be associated with the presence of a certain amount of aluminium; it is possible that a new peak has been inserted between 250° and 300° K. which has had the effect of smoothing out the curve in this way. The more general significance of these results will be considered later.

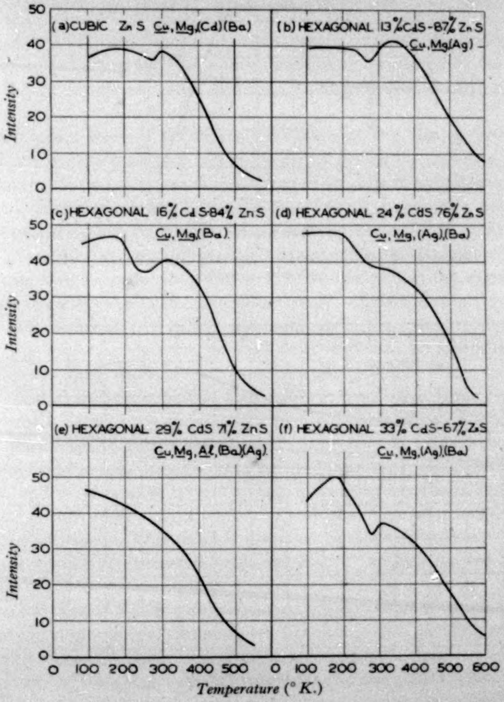


Figure 3.

Meanwhile it remains to indicate the results on two rather different types of luminescent material; for it was felt advisable even at this stage that experiments on as many different types as possible would be of help in the general interpretation. Figure 4 shows the effect of temperature on the fluorescence of cadmium iodide activated by lead, with minor traces of Ag and Cu present. The intensity is fairly constant at low temperatures but this is followed by a steep and linear fall at about 200° K.

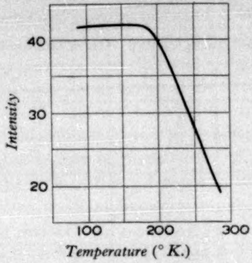


Figure 4. Cadmium iodide, CdI_2; impurities Pb, (Ag), (Cu); yellow fluorescence.

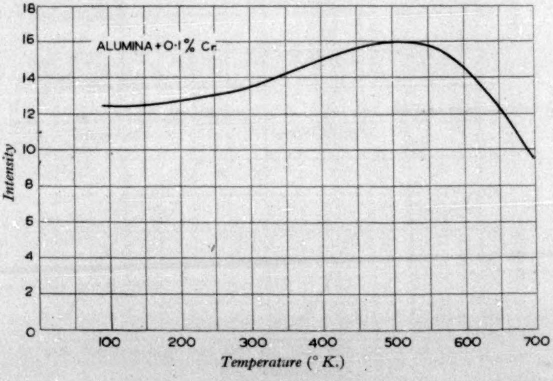


Figure 5. Alumina activated by chromium.

So far, luminescent materials with the broad structureless type of band spectrum only have been considered. In figure 5 is given the curve for alumina activated by chromium. The luminescence spectrum of this material taken at room temperatures consists of a number of rather broad lines together with a rather weak intensity general background. The lines have been attributed by Tomaschek and

Deutschbein to triply ionized chromium. The intensity curve is somewhat similar to that of the hexagonal zinc sulphide of figure 1, except for the rather flat portion at low temperatures. It should also be noted that the maximum in the curve occurs at a much higher temperature, viz. 500° K., than for any others so far examined.

§4. DISCUSSION OF RESULTS

While it must be stressed that the present results are only the preliminaries of a rather wider investigation and that minor details may be altered by further work, it is felt that some points of rather general significance may already be deduced from them.

In the first place there is no strong evidence that the change from cubic to hexagonal zinc sulphide produces any marked changes in the intensity curves. It has already been pointed out that the intensity of the low temperature peak of the zinc-cadmium sulphides relative to that of the "high" temperature peak depends to a marked extent on the proportion of cadmium present. This could clearly be ascribed to the gradually changing lattice constant as the amount of cadmium increases, were it not for the fact that in the zinc sulphides the same low temperature peak, present on a rather diminished scale, appears also to depend on the presence of cadmium not as a bulk constituent, as in the solid-solution, but as a minor impurity. This low temperature peak must therefore be associated with the cadmium, and the suggestion is, that even in those powders where the cadmium is already present in bulk, the cadmium, possibly in some other form, is also acting as an important impurity from the point of view of fluorescence. There is nothing particularly objectionable in this idea, as it has been used to explain the behaviour of certain semi-conductors. It is however new as far as the subject of luminescence is concerned, and it remains to be seen what is the exact significance physically of the association of the cadmium as an impurity with the so-called principle activators such as copper and silver. This point is particularly interesting in view of the fact that the X-ray results for the solid-solutions record the definite presence of inhomogeneities.

The curves of figures 2 and 3 were obtained prior to those of figure 1, and their strangely varying slopes at low temperatures were somewhat puzzling at first sight.

The results shown in figure 1, however, together with those on alumina and the known nature of the spectra of the materials, give the general clue.

The susceptibility of all luminescent sulphides to traces of extraneous impurity leads to the presence, in general, of more than one broad band in the fluorescence spectrum. In figures 2 and 3 we appear to be witnessing the superposition of the temperature curves for more than one band. Occasionally, when it is possible to produce a powder with one chief activating impurity, a decidedly simple type of temperature curve results, and this simplicity is shown in figures 1 and 5 in spite of the rather different types of spectra.

It is interesting that all the substances examined show on the high temperature side a rather steep slope, and this rather confirms our view. From the theoretical standpoint there is presumably no difficulty in accounting for the presence of a number of fluorescence bands. One of the problems will be to account for the dependence of the band intensity on temperature, the chief characteristics being a positive slope at low temperatures, followed by a negative slope at higher values of T. At the present time it appears rather easier to understand the high temperature part of the curve. As the temperature increases a decreasing fraction of the total number of excited electrons becomes available for radiative transitions to lower levels. There is at present no evidence to show whether these electrons remain in the upper band, or whether their energy is increasingly lost by collision with lattice atoms as the temperature rises. From the experimental standpoint it is important to determine to what extent the absorption of ultra-violet remains constant over the temperature range considered. I am indebted to Dr Peierls for pointing out the two aspects of this problem: the possible variation of average absorption with temperature, and the dependence of absorption on the nature of the exciting spectrum. Until answers concerning these points have been obtained, no further certain conclusions may be reached from the present experiments.

REFERENCES

(1) SHOCKLEY, W. *Phys. Rev.* **50**, 754 (1936).
(2) EWING, D. H. and SEITZ, F. *Phys. Rev.* **50**, 760 (1936).
(3) HILSCH, R. Page 40 of this volume.
(4) See, for example, *Handbuch der Experimental Physik*, **23**, (1927).
(5) SPEDDING, F. H. *Phys. Rev.* **50**, 574 (1936), **46**, 975 (1934).
(6) RANDALL, J. T. *J. Roy. Soc. Arts*, **85**, 354 (1937).
(7) SCHLEEDE, A. *Angewandte Chemie*, **48**, no. 19, 277 (1935).

DISCUSSION OF THE PAPERS BY HILSCH AND RANDALL

Reported by N. F. MOTT

IN reply to questions, Dr Hilsch emphasized that photoconductivity was observed in sulphide phosphors, but not in the alkali halides. But in the latter case photoconductivity did not seem to be intimately connected with phosphorescence; the electrons are not removed to any very large distances. Prof. Pohl suggested that *if* there exists a phosphorescence with a long decay period, *then* we may suppose that the electron responsible for the radiation is removed by the absorbed quantum a long way from its original position, i.e. a distance of many atomic diameters. But in the other type of phosphor, in which the electron is not removed, the light absorption causes the transformation of one type of molecule into another; the initial and final states being distinguished for instance by a difference of crystal form—i.e. by the atomic nuclei taking up new positions. Prof. Pohl also emphasized the importance of making large crystals of the sulphide phosphors in order to understand their properties.

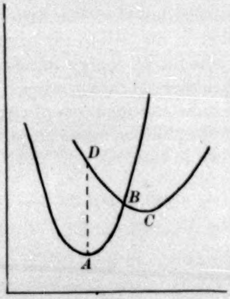


Figure 1.

Prof. Mott and Dr de Boer discussed the mechanism by means of which a molecule in a crystal could re-emit light after a period of minutes or hours. Figure 1 shows the energy of the normal and excited states of the molecule plotted against some parameter d representing the configuration of the atoms of the molecule; for example, the distance between two of the atoms. A molecule originally in the state A absorbs, by the Franck-Condon principle, light having the quantum energy AD. The molecule then moves into the more stable state C, in which it cannot radiate.

Thermal agitation might cause the molecule to come into the state *A*, whence it could descend to *A* giving up its excess energy as heat, or, owing to the finite velocity of motion of the ions, it might ascend towards *D* and thus have a chance to radiate. The resulting band would however have its maximum at very large wave-lengths.

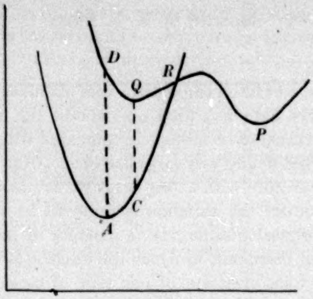


Figure 2.

The more complicated mechanism shown in figure 2 seems necessary in order to account for an emission band in the visible, the upper curve having two minima. After absorption the large amount of energy released takes the molecule to *P*, where it cannot radiate. If then thermal energy raises it to *R*, it will drop down to *Q*, where it will remain until it radiates a quantum of energy *QC*.

Mr J. Ewles gave an account of experiments on phosphorescence carried out at Leeds. These will be published in the *Proc. roy. Soc.**

---

* See also Ewles, *Proc. roy. Soc.* A, **129**, 509 (1931), *Proc. Leeds Phil. Soc.* **3**, 277 (1936).

SEMI-CONDUCTORS WITH PARTIALLY AND WITH COMPLETELY FILLED 3*d*-LATTICE BANDS

By J. H. DE BOER and E. J. W. VERWEY,
Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken,
Eindhoven, Holland

ABSTRACT. Attention is drawn to a class of semi-conductors or insulators with incompletely filled 3*d* bands. Their lack of conductivity, if the number of electrons per atom is an integer, is explained by the circumstance that a moving electron will have a large probability of being withdrawn to the initial atom, if only the potential barriers to be penetrated are sufficiently high to reduce the frequency of transition below a certain limit. This inhibiting factor disappears, if for ions of equal electronic levels the number of electrons per atom differs from an integer. In the case of NiO this condition is fulfilled if an electron is brought by thermal excitation from the lattice 3*d* band into the somewhat raised and less occupied levels *a*, *a*′ (figure 1); these levels belong to Ni ions adjacent to a vacant Ni lattice point introduced by the deviations from stoichiometry, and two of these Ni ions are at the absolute zero Ni^{3+} ions. An analogous conduction mechanism holds for non-stoichiometric Cu_2O, with a completely filled 3*d* band (figure 2).

Photoconductivity is generally observed with substances with completely filled zones and never with substances of the NiO type. A tentative explanation is given for this fact on the basis of the model of figure 1 and figure 2.

In non-stoechiometric ZnO vacant oxygen lattice points are assumed (figure 3); in that case the calculation of the lattice levels shows that at the lattice holes one Zn^{2+} is converted into Zn, whereas in the lattice the additional electrons form Zn^+ ions, as will be the case after thermal transitions of the electrons belonging to these Zn atoms into the lattice 4*s* band.

---

§1. CLASSIFICATION OF SEMI-CONDUCTORS

According to the quantum theory of electronic states in solids, as developed by Sommerfeld, Bloch, Brillouin, Bethe and others(1, 2, 3), with the special aim of understanding the electrical properties of the metals, those substances will be electrical insulators for which the number of electrons is just sufficient to fill up a number of Brillouin zones completely, and the lowest unoccupied Brillouin zone is separated from the occupied zone with the highest energy by a sufficiently broad energy gap (forbidden region). For instance the following ionic compounds NaCl, MgO, AgCl, ZnO, TlCl all contain only ions with closed electronic groups or sub groups and thus only completely filled Brillouin zones, and they are known to be very poor conductors if they are pure and of stoichiometric composition. Though, according to quantum mechanics, all the electrons of a perfect lattice are more or less free to move through the lattice, the electronic states of a completely filled energy zone cannot give rise to electronic conduction, and unidirectional transport of electrons is only possible if a zone is incompletely filled, either because the number of electrons is incapable of filling up the zones completely, or because several zones overlap in the lattice, the electrons of one atomic level being thus distributed over more than one band or zone of lattice levels. On the basis of these conceptions Wilson(4) and Fowler(5) have developed a theory of semi-conductors. Wilson considers the case of two energy zones, one exactly full of electrons at absolute zero and a higher one entirely empty, separated by a narrow forbidden region. Accordingly at a higher temperature there will be a few electrons of the lower zone in the higher one, and necessarily a number of empty states in the lower zone. Both will give rise to electronic conduction, but predominantly the electrons in the higher zone, where the potential barriers are lower with respect to the electronic levels. Such semi-conductors, which owe their conductivity to thermal excitation of electrons from one energy zone into another higher one, were called *intrinsic* semi-conductors.

A substance belonging to the class of semi-conductors in which electronic conduction occurs predominantly according to the model of Wilson is probably Cu_2O of stoichiometric composition. In this compound the cuprous ion Cu^+ contains a closed $3d$ shell and an empty $4s$ shell.

Sometimes insulators of the type considered above can be converted into semi-conductors in two ways, either by small deviations from stoichiometric composition or by foreign impurities. Of these *extrinsic* semi-conductors only the first mentioned will be considered in the present discussion.

(*a*) There exists, however, a large class of semi-conductors of a quite different type, for which it has only been recognized incidentally that they must be treated in a way deviating fundamentally from the Wilson theory. Several substances contain atoms or ions with an odd number of electrons; then, in many cases, at any rate for substances with a simple lattice type (such as simple translation lattices, or lattices with a face centred or body centred unit cell), the amount of electrons is incapable of filling up a number of Brillouin zones completely and we have to deal with a partially occupied Brillouin zone. Nevertheless several substances, especially ionic compounds, of this type do not show a metallic conductivity, but belong to the class of semi-conductors or even insulators.

In the present paper we will restrict ourselves to compounds containing ions of the first long series of the periodic system. As examples may be mentioned MnO ($\log \rho = 8$), CoO ($\log \rho = 8$), Mn_3O_4 ($\log \rho = 7$), Fe_2O_3 ($\log \rho = 10$), CuO ($\log \rho = 7$), etc.* The electronic configurations of the cations involved can be read from table 1. This table, comprising elements which have the argon configuration $(1s)^2; (2s)^2 (2p)^6; (3s)^2 (3p)^6$ in common, shows the distribution of electrons between the $3d$ and $4s$ shells for a number of important atoms and ions from the part of the periodic system considered. These distributions can be derived in some cases from the spectroscopical data(6) concerning the ground state of the free atoms or ions (shown in bold-faced type) and the remainder can then be derived by interpolation or (and) by taking into account the paramagnetism of the ions in the corresponding salts(7). From table 1 it results that all ions present in stable chemical compounds in the transition region of the periodic system considered contain $3d$ electrons and no $4s$ electrons. As a consequence of this circumstance we infer that there is no great difference between substances like those mentioned above, containing odd numbers of electrons, and for instance NiO, with even numbers of electrons, since the band of $3d$ levels contains five $3d$ zones and these $3d$ levels, coinciding in the free ions, presumably are not split up wholly into separate zones in the lattice, and all ions with an incompletely filled $3d$ group will therefore give rise to partially occupied energy bands in the lattice. Actually there is no great difference in the behaviour of CoO and NiO; for the latter also $\log \rho = 8$.

---

* The $\log_{10} \rho$ values (ρ = specific resistance in ohm-cm.) are only given as integers because of the inevitable uncertainty in these data; for our considerations only the order of magnitude is significant.

Table I

Atomic number of atoms / mber of ectrons in ion	18	19	20	21	22	23	24	25	26	27	28
	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$
18	Ar 0 0	K^+ 0 0	Ca^{2+} 0 0	Sc^{3+} 0 0	Ti^{4+} 0 0	V^{5+} 0 0					
19		K 0 1			Ti^{3+} 1 0	V^{4+} 1 0					
20			Ca 0 2		Ti^{2+} 2 0	V^{3+} 2 0					
21				Sc 1 2	Ti^+ (2) (1)	V^{2+} 3 0	Cr^{3+} 3 0	Mn^{4+} 3 0			
22					Ti 2 2	V^+ 4 0	Cr^{2+} 4 0	Mn^{3+} 4 0			
23						V 3 2	Cr^+ 5 0	Mn^{2+} 5 0	Fe^{3+} 5 0	Co^{4+} 5 0	
24							Cr 5 1	Mn^+ 5 1	Fe^{2+} 6 0	Co^{3+} 6 0	Ni^{4+} 6 0
25								Mn 5 2	Fe^+ 6 1	Co^{2+} 7 0	Ni^{3+} 7 0
26									Fe 6 2	Co^+ 8 0	Ni^{2+} 8 0
27										Co 7 2	Ni^+ 9 0
28											Ni 8 2

(*b*) Not all substances of the type considered are poor conductors. It is a well-known fact that both the conductivities of Cu_2O, CuJ, ZnO (with cations having a complete $3d$ shell, $3d^{10}$) and of CoO, NiO etc. (incomplete $3d$ shell) can be raised several powers of ten by small deviations from the stoichiometric composition[8, 9, 10, 11] and it has already been suggested by Wagner that this increased conductivity is connected with quasi-free electrons or electron holes owing to the presence of ions of higher or lower valency. A very interesting case is represented by Fe_3O_4 ($\log \rho = -2$), which has a conductivity of about ten powers of ten as high as Mn_3O_4, Co_3O_4, $\gamma\, Mn_2O_3$, $\gamma\, Fe_2O_3$.

In a previous publication we have shown that the cation arrangement in the lattice of Fe_3O_4 shows an "averaged structure" of a special type, viz. a statistical distribution of equal amounts of Fe^{2+} and Fe^{3+} ions about crystallographically identical lattice points(12, 13); in this respect it differs from Co_3O_4, $\gamma\ Fe_2O_3$, etc. with otherwise identical or closely related crystal structures (spinel type). From this we infer that favourable conditions for electronic conduction exist, if for a band of electronic states the number of electrons per atom (ion) differs from an integer, and this is also important in relation to the conductivity of non-stoichiometric compounds.

(*c*) A third point, which seems to be of some importance for a comprehension of the behaviour of the substances considered, is that only those substances (stoichiometric and non-stoichiometric) show photo-conductivity, which are derived from compounds with cations containing a complete 3*d* shell, viz. CuJ, Cu_2O, ZnO. This seems to be a general rule throughout the whole periodic system, since all substances reported to be photoconductors (halides of the alkali- and alkaline earth metals and of Ag^+, Cu^+, Tl^+, Hg^{2+}, Pb^{2+}; very many sulphides, e.g. Ag_2S, Sb_2S_3, HgS, Bi_2S_3, PbS, Ag_3SbS_3; oxides like BaO, Cu_2O, Ag_2O, CdO, Sb_2O_3) contain cations (and anions) with closed electronic groups or sub-groups. No photoconductivity has been observed, as far as we know, for substances like MnO, CoO, NiO, Co_3O_4, Mn_3O_4, Fe_2O_3 etc.; in this laboratory Mr H. H. Kraak has investigated certain of these compounds* by irradiation with a high pressure mercury discharge lamp and has been unable to establish any effect upon their conductivity.

From this discussion, then, a number of interesting points result, which can be summarized in the following three problems:

(1) Why are several of the oxides considered here semi-conductors or almost insulators, although they contain an incompletely occupied 3*d* band?

(2) Why do exceptionally favourable conditions for electronic conduction arise if the number of electrons per atom in this band is different from an integer?

(3) What is the reason why all these substances do not show photoconductivity, whereas those substances containing a completely filled 3*d* band are all photoconductors?

In the following sections we shall consider these substances from the point of view of their electronic bands and the relations between them.

§2. LATTICE DEFECTS

The nature of the lattice deviations involved in deviations from the stoechiometric composition and their significance for electronic conduction have been discussed in detail by Wagner(10). Also in our case we must consider beforehand what changes occur in the lattices of the substances investigated, if the composition is made different from stoichiometry. For our present purpose, we need not consider the small deviations from the perfect lattice, which are present in every real lattice owing to the thermal equilibrium corresponding to the previous thermal history(14).

---

* Namely NiO, NiO containing some oxygen in excess, Co_3O_4 and Mn_3O_4 as pressed bars.

Greenish NiO can be transformed by oxidation into black "NiO" and then contains a small amount of oxygen (e.g. 0·5 per cent) in excess. The extra oxygen may be located between the normal lattice ions (interlattice points), but owing to the small polarizability of the oxygen it is much more likely that the lattice contains vacant nickel lattice points, whereas the additional oxygen is located at normal lattice points. This view is substantiated by the work of Jette and Foote(15), who investigated the crystal structure of Wüstite ("FeO"). A phase of pure FeO is not stable under any conditions; for the Wüstite phase, if prepared at 1050°, they found solid solutions containing 76·7–76·1 per cent Fe, i.e. from $Fe_{0\cdot94}O$ to $Fe_{0\cdot91}O$. These phases contain vacant positions in their cation lattice; the latter phase for example contains therefore an averaged distribution of $\frac{8}{11}$ Fe^{2+}, $\frac{2}{11}$ Fe^{3+} and $\frac{1}{11}$ vacant lattice points per oxygen ion about the normal cation position.* Also pure NiO seems to be unstable(16), and identical relations may be expected here, though the deviations from stoichiometry are less than in the case of FeO.

For NiO with an oxygen excess we must therefore assume vacant points in the cation lattice. Such an assumption can also safely be made for the case of CuJ with a small excess of iodine, in view of the large radius of the J^- ion. For Cu_2O the same view has been advocated by Dünwald and Wagner(17). It has generally been assumed in these substances containing a metal deficit that the excess of negative charge originating from the excess of anions is neutralized at the cations, i.e. by the formation of cations of higher valency (Fe^{3+}, Ni^{3+}, Cu^{2+}); in the present cases this conception seems quite reasonable on the basis of chemical arguments, but the possibility that anions of a lower charge (eventually neutral atoms) are formed cannot be excluded *a priori*. Indeed, in KJ containing a small excess of iodine, no K^{2+} ions but J atoms are formed. This can easily be ascertained, however, for every case, by considering to what extent the various electronic levels are shifted in the lattices: the electrons will be removed from the *highest occupied* level. The results of such calculations are summarized in table 2. These calculations yield, of course, the positions that the levels would have, if they were not broadened by the lattice (in the following we denote these positions as "centres" of the bands). We also include the calculations of the electronic levels of ions adjacent to a vacant lattice point, for electrons must be removed as a consequence of the disappearance of a number of cations from the lattice and it is generally more favourable to remove these electrons from a cation that is adjacent to such a lattice hole. For the case of Cu_2O Schottky and Waibel(18) assumed therefore that Cu^{2+} ions are located directly adjacent to a vacant Cu^+ lattice position. For instance, for NiO (NaCl lattice type), where each vacant Ni point is surrounded by 12 nickel ions, we wish to consider the case that two of these nickel ions yield an electron and become Ni^{3+} ions, in order to counterbalance the absent Ni^{2+}. Neglecting polarization energies we see that such a Ni^{3+} is surrounded by a normal lattice minus one Ni^{2+} at a distance $r\sqrt{2}$ (r = shortest Ni-O distance) and plus one positive charge at $2r\sqrt{2}$ (in the most favourable state), hence the *Madelung* energy for one electron at the lattice point considered (Ni^{3+} ion

---

* Another possibility is that the Fe^{3+} seek different interstices, but presumably it can be excluded by the fact that no complete series of solid solutions with Fe_3O_4 exists.

Table 2

NiO			
Lattice type: NaCl,	$a=4{\cdot}17$ A.	*Lattice:*	
Shortest distance Ni to O	$=2{\cdot}09$ A.	*Madelung* energy (M)	$=\ 24{\cdot}2$ V.
Distance Ni^{3+} to lattice hole	$=2{\cdot}98$ A.	Level Ni^{2+} $3d=M-I_3$	$=-\ 6$ V.
Distance Ni^{3+} to Ni^{3+}	$=5{\cdot}96$ A.	Level O^{2-} $2p=-M-E_2$	$=-14$ V.
Madelung constant	$=1{\cdot}748$		
Third ionization energy Ni (I_3)	$=$*ca.* 30 V.	*At lattice hole:*	
Second electron affinity O (E_2)	$=-10$ V.	*Madelung* energy Ni^{2+} (M'_{Ni})	$=31{\cdot}6$ V.
		Madelung energy O^{2-} (M'_O)*	$=13{\cdot}8$ V.
		Level Ni^{2+} $3d=M_{Ni}'-I_3$	$=+1$ V.
		Level O^{2-} $2p=-M_O'-E_2$	$=-3{\cdot}8$ V.
CuJ			
Lattice type: cubic ZnS,	$a=6{\cdot}05$ A.	*Lattice:*	
Shortest distance Cu^+ to $J^-=\frac{1}{4}a\sqrt{3}$	$=2{\cdot}62$ A.	*Madelung* energy (M)	$=\ 9{\cdot}0$ V.
Distance Cu^+ to lattice hole $=\frac{1}{2}a\sqrt{2}$	$=4{\cdot}27$ A.	Level Cu $4s=M-I_1$	$=+\ 1{\cdot}2$ V.
Madelung constant	$=1{\cdot}639$	Level Cu^+ $3d=M-I_2$	$=-11{\cdot}2$ V.
First ionization energy Cu (I_1)	$=\ 7{\cdot}8$ V.	Level J^- $5p=-M-E$	$=-12{\cdot}1$ V.
Second ionization energy Cu (I_2)	$=20{\cdot}2$ V.		
Electron affinity J (E)	$-3{\cdot}1$ V.	*At lattice hole:*	
		Madelung energy Cu^+ (M'_{Cu})	$=12{\cdot}4$ V.
		Madelung energy J^- (M'_J)	$=\ 3{\cdot}5$ V.
		Level Cu^+ $3d=M'_{Cu}-I_2$	$=-\ 7{\cdot}8$ V.
		Level J^- $5p=-M'_J-E$	$=-\ 6{\cdot}6$ V.
ZnO			
Lattice type: hexagonal ZnS,	$a=3{\cdot}25$ A.	*Lattice:*	
	$c=5{\cdot}23$ A.	*Madelung* energy (M)	$=\ 23{\cdot}9$ V.
Shortest distance Zn to O	$=1{\cdot}98$ A.	Level Zn^+ $4s=M-I_2$	$=\ 6{\cdot}0$ V.
Distance Zn to Zn	$=3{\cdot}25$ A.	Level Zn $4s=2M-I_1-I_2$†	$=\ 20{\cdot}5$ V.
Madelung constant	$=1{\cdot}639$	Level $O^{2-}=-M-E$	$=-13{\cdot}9$ V.
First ionization energy Zn (I_1)	$=9{\cdot}4$ V.	Lowest member	
Second ionization energy Zn (I_2)	$=17{\cdot}9$ V.	$O^{3-}>-13{\cdot}9+\frac{2\epsilon^2}{r_{O^{2-}}}$‡	$=>8$ V.
		At lattice hole:	
		Madelung energy Zn^+ (M')§	$=+13{\cdot}7$ V.
		Madelung energy Zn (M'')	$=+\ 9{\cdot}3$ V.
		Level Zn^+ $4s=M'-I_2$	$=-\ 4{\cdot}2$ V.
		Level Zn $4s=2M''-I_1-I_2$	$=-\ 8{\cdot}7$ V.
KJ			
Lattice type: cubic NaCl,	$a=7{\cdot}05$ A.	*Lattice:*	
Madelung constant	$=1{\cdot}748$	*Madelung* energy (M)	$=\ 7{\cdot}2$ V.
Distance K to J	$=3{\cdot}53$ A.	Level K^+: $M-I_2$	$=-24{\cdot}5$ V.
Distance K to $K=\frac{1}{2}a\sqrt{2}$	$=4{\cdot}99$ A.	Level J^-: $-M-E$	$=-10{\cdot}3$ V.
Second ionization energy K (I_2)	$=31{\cdot}7$ V.		
		Adjacent to failing K^+	
		Madelung energy K^+ (M')	$=\ 10{\cdot}1$ V.
		Level K^+: $M'-I_2$	$=-21{\cdot}6$ V.
		Madelung energy J^- (M'')	$=\ 3{\cdot}1$ V.
		Level J^-: $M''-E$	$=-\ 6{\cdot}2$ V.

* For two O^- ions adjacent to a vacant Ni^{2+} lattice point.

† For two electrons at one Zn^{2+} lattice ion.

‡ If an electron is added to O^{2-} there are no discrete levels; the lowest member of the continuum will be at least $2\epsilon^2/r_{C^{2-}}=22$ V. higher ($r_{O^{2-}}=1{\cdot}3$ A. = radius of O^{2-}).

§ For two Zn^+ ions adjacent to a vacant oxygen lattice point.

adjacent to a vacant Ni^{2+} point) amounts to (A = *Madelung* constant):

$$\frac{2A\epsilon^2}{r}+\frac{2\epsilon^2}{r\sqrt{2}}-\frac{\epsilon^2}{2r\sqrt{2}}=24\cdot2+9\cdot8-2\cdot4=31\cdot6 \text{ volts}$$

The electronic level of these ions is therefore raised 7·4 volts with respect to normal lattice ions, or rather considerably less owing to several polarization effects. The other data are calculated in a similar way.

In the case of ZnO the deviation from stoichiometry causing electronic conductivity is an excess of Zn. In the analogous case of BaO it has been shown that the red BaO containing an excess of about 1 per cent Ba has a density of about 0·5 per cent less than that of normal BaO(19). We will therefore assume in BaO and similar substances that the excess of metal is present at normal lattice points, whereas a number of oxygen lattice points is vacant, though, for the case of ZnO, the possibility cannot wholly be excluded that Zn takes interlattice points, since Zn is more polarizable than Ba, and ZnO has a different lattice type. In the case of ZnO extra electrons must be introduced and we must therefore consider the *lowest unoccupied* level in the lattice and at lattice holes. From table 2 we make the following inferences.

For NiO with oxygen excess: both in the normal lattices as well as at lattice holes the removal of electrons leads to Ni^{3+} ions and never to O^{-} ions.

For CuJ with iodine excess: in the normal lattice Cu^{2+} are formed; adjacent to vacant Cu^{+} lattice points the highest occupied level seems to be J^{-} and therefore J atoms are formed; the latter conclusion is somewhat uncertain owing to the high polarizabilities of the ions involved.

For ZnO with metal excess, assuming vacant oxygen lattice points: adjacent to an absent O^{2-} ion the lowest unoccupied level is that for a Zn atom. In the regular lattice, however, an excess of electrons yields a more uniform distribution of the electrons and leads to Zn^{+} ions. The formation of O^{3-} can be excluded.

For KJ with iodine excess: the electrons are always removed from J^{-} ions.

§3. MECHANISM OF CONDUCTION

We now proceed to a consideration of the mechanism of electronic conduction. The theory of electronic states in metals has been developed on the basis of the assumption that the interaction of the electrons and ions of the lattice can be approached by treating each electron as moving in the field of the ions and the average field of all other electrons. This method of approach implies that all atoms (ions) of a definite kind contain an equal number of electrons, or, since electron movement must necessarily alter the number of electrons of an atom temporarily, that local charge differences are neutralized by other electrons within a short time; in other words that the electrons are free to such an extent that they can still be considered as *not* belonging to definite atoms. If the potential barrier between the atoms (ions) of one kind is increased the probability of interchange of electrons decreases rapidly and the time lag mentioned above increases. Thus, for somewhat higher potential barriers the state of affairs is finally fundamentally different in metallic conduction. There is a certain probability that an electron leaks through a potential barrier to a neighbouring atom, say from one Ni^{2+} to another Ni^{2+} in pure NiO. The immediate result is that in a row of Ni^{2+} ions two adjacent Ni^{2+} ions are changed into Ni^{+} and Ni^{3+}. If the excess of positive charge at the Ni^{3+} ions is not sufficiently rapidly neutralized by other electrons the probability is high that the electron at the Ni^{+} ions does not travel further into the lattice, but moves back, even against the force resulting from the applied electrical field, to the original atom. The theoretical treatment of the electronic movement will obviously be quite different from that in the theory of metals and must consist of a discussion of the probability of the existence and prevalence of such charge disturbances and the chance of propagating the electrons from them to other similar disturbances. In default of such a treatment we may provisionally infer that the nature of such an electronic conduction mechanism probably implies that in a certain region the conductivity will be highly sensitive to the height of the potential barriers. Substances with partially filled energy zones will therefore, according to this qualitative picture, generally be either metals or poor conductors, whereas intermediate cases will probably be rare. Substances of the latter intermediate type,i.e. semi-conductors with appreciable conductivity, will, however, be rather interesting, since one might expect their conductivities to be very sensitive to changes in the lattice spacings and thus to the situation of the bands with respect to the potential barriers, and therefore, not only to temperature, but also to external pressure, formation of solid solutions etc.

The existence of semi-conductors or insulators with partially filled energy zones, could not, indeed, be properly understood from the viewpoint of the present theory of electronic states for metals(20, 21). A peculiar difficulty was also offered by a substance like Fe_3O_4, for according to these views one could not immediately explain why a substance with a partially filled $3d$ band containing $5\frac{1}{2}$ electrons per Fe atom should conduct 10^{11} times as well as a substance of the same lattice type and practically identical lattice dimensions with a partially filled $3d$ band containing 5 electrons per Fe atom (γ Fe_2O_3). Similar arguments hold for the non-stoichiometric compounds. For these substances the Wilson model for extrinsic semi-conductors(4), eventually the modified model of de Boer and van Geel(22), cannot be applied. According to this theory, semiconduction has been explained by discrete impurity levels; if energy is taken up from the thermal movement, electron transitions are assumed to occur from these levels to a normally completely empty band, or from a completely filled band to empty impurity levels. In the cases under consideration, however, this mechanism cannot help us, since the energy band ($3d$) is partially filled with electrons in the stoichiometric compounds as well as in the non-stoichiometric ones; and it cannot explain the considerable increase in the conductivity if the substance no longer contains a whole number of electrons per ion.

Our consideration given above showing that substances with partially filled energy bands must actually be expected to be poor conductors, if only the potential barriers are sufficiently high to reduce the frequency of interchange below a certain limit, which, for instance, can be of the order of the inverse of the duration of an "excited lattice state" (in our example $Ni^{+}-Ni^{3+}$), explains immediately the effect of a non-integral number of electrons per atom in a band, or, in other words, of an average structure of a cation lattice with unequally charged ions (or in part atoms) of the same element. If, for instance, in Fe_3O_4 an electron moves from a Fe^{2+} ion to a Fe^{3+} ion at an equivalent lattice point, the initial ion is transformed into Fe^{3+} and the accepting ion into Fe^{2+}. As a consequence of this reaction (indicated according to Wagner by $Fe^{2+}+Fe^{3+}\rightarrow Fe^{3+}+Fe^{2+}$), if only it occurs simultaneously at several points in the lattice, no fundamental change in the statistical distribution of Fe^{2+} and Fe^{3+} has occurred. The essential difference from the foregoing case is that the electronic movement does not automatically imply the appearance of a charge disturbance inhibiting further electronic transport. In a perfect Fe_3O_4 crystal the chain of electronic interchanges is only broken down at the surface of the crystals. Since after each electronic transition the energy state of the lattice is not altered (except for minor effects), the amount of energy necessary for each electron transition is very small. Such a lattice with a statistical distribution of unequally charged homonymous ions shows therefore a high conductivity and a low temperature coefficient.

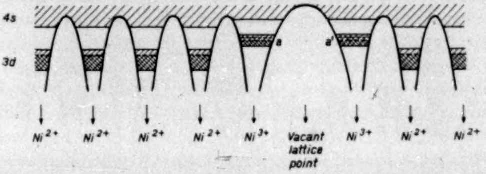


Figure 1. Schematic representation of the $3d$ and $4s$ band in a substance like NiO, containing a small amount of oxygen in excess. Section through a row of Ni^{2+} ions (110 direction) with one absent cation.

Let us now consider the periodic potential field along a row of cations (in a face-centred lattice, therefore a (110) direction) in a substance with a partially filled $3d$ band like NiO, disturbed at one point by the absence of one cation (figure 1).* At absolute zero two of the only slightly broadened levels of the Ni ions adjacent to the lattice hole (in the three-dimensional lattice there are 12 such ions), a and a', contain one electron less than the normal lattice ions. The partially filled $3d$ band of the normal lattice ions does not give rise to any appreciable conduction owing to the effect of the potential barriers, as considered above. Electronic interchange takes place easily only between the 12 cations adjacent to the lattice hole sharing 10 electrons, but this does not lead to any transport of electricity in an electric field. The $4s$ band especially is strongly broadened by the lattice, but the bands are still separated by a considerable forbidden energy region. Actually pure NiO does not absorb strongly in the region of visible light; its colour is a light yellowish green.

---

* Strictly speaking also the second nearest neighbours, etc. of a lattice hole have slightly raised levels, and also the potential barriers are slightly changed. The schematic picture of figures 1–3, however, is sufficient for our purpose.

The forbidden region can therefore be estimated to be somewhat less than 3 volts, Upon introduction of a small excess of oxygen, however, the colour turns into black, which is probably connected with transitions from the raised levels *a*, *a'* into the empty 4*s* zone of the lattice. The introduction of an excess of oxygen, i.e. of a number of levels *a*, *a'* (being partially Ni^{3+} ions, namely $\frac{1}{6}$ of them), simultaneously increases the conductivity, of which the mechanism can now be understood in the following way. If the temperature is above absolute zero there is a certain probability that a normal lattice Ni^{2+} ion gives off its electron to one of the Ni^{3+} ions adjacent to the lattice hole, for which transition an amount of energy must be supplied from the thermal movements in order to bring the electron into the higher levels *a*, *a'*. The result is that a row of normal lattice ions contains a Ni^{3+} ion of the same energy level as the Ni^{2+} ions, and conditions as considered for the case of Fe_3O_4 are created. Hence a chain of transitions $Ni^{2+} + Ni^{3+} \rightarrow Ni^{3+} + Ni^{2+}$ sets in, which, in the presence of an electric field, leads to electronic conduction. If during such a chain of transitions the electronic deficit propagated through the lattice meets a lattice hole, i.e. when a Ni^{2+} ion in the neighbourhood of such a hole is converted into a Ni^{3+}, there is a large probability that an electron of a level *a* (*a'*) falls back to this ion, and the chain of transitions is broken down; every new chain must start again with a jump of an electron to a non-occupied level of a Ni^{3+} ion adjacent to a lattice hole. In this way an equilibrium is established, and the total number of Ni^{3+} ions at normal lattice points, and therefore the conductivity, depends on the temperature according to a Boltzmann partition law.

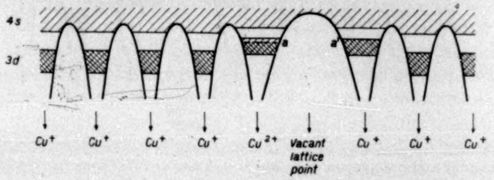


Figure 2. Schematic representation of the 3*d* and 4*s* band in a substance like Cu_2O, containing a small amount of oxygen in excess. Section through a row of Cu^+ ions with one absent cation.

In the case of Cu_2O or CuJ the picture is somewhat different owing to the fact that here the band of 3*d* electrons is completely occupied. Figure 2 shows again the case of a row of Cu^+ ions and one absent cation. In this case one of the cations directly surrounding the lattice hole (in figure 2 there are only two, again represented by somewhat raised levels *a* and *a'*) contains one electron less (Cu^{2+} ion). The red colour of Cu_2O indicates that the Cu^+ 3*s* and the Cu 4*s* zone are separated by a forbidden zone of about 2 volts (the spectral photoelectric region, according to this transition, lies at about 630 mμ. corresponding to about 2 volts); the "centre" of the latter lies 12·4 volts higher than that of the former (§ 2, table 2). At absolute zero no conduction is possible, since the 3*d* band is completely occupied and the 4*s* zone is entirely empty. At higher temperature three conductivity mechanisms are possible:

(1) Electron transitions from $3d$ into $4s$.

(2) Electron transitions from levels a, a' etc. into the $4s$ zone.

(3) Electron transitions from the $3d$ band into the level a.

(1) leads to electronic movement of an electron in $4s$ and of an electron hole in $3d$, the former predominating; (2) leads only to the former, whereas electron transitions (3) imply defect conductivity in $3d$. According to measurements(18) of the Hall constant and measurements of the thermo-e.m.f.(17) of Cu_2O containing a small excess of oxygen this substance shows defect conductivity and therefore obviously the third mechanism prevails. If, however, the Cu_2O is heated in a high vacuum, the substance thus obtained, which will be now close to the stoichiometric composition, is still an electron hole conductor at lower temperatures, but above 500° it shows a negative Hall constant. Obviously the number of Cu^{2+} ions at levels a etc. is so small now that at higher temperatures mechanisms (1) and (2), owing to their larger temperature coefficient, will finally predominate over (3), whereas at lower temperatures the activation energy of (1) and (2) are too high to yield an important conductivity. It should be pointed out that the number of lattice holes of the type of figure 2 will be larger than the number of Cu^{2+} ions at such lattice holes, owing to thermal lattice deviations at the temperature at which the crystal was formed (Schottky-Fehlstellen); all such levels at lattice holes can contribute to mechanism (2), whereas only an unoccupied level a can contribute to mechanism (3). In pure Cu_2O all copper ions are Cu^+ ions and therefore only (1) and (2) should be possible.

With increasing amount of excess oxygen ions the mutual influence of the various lattice holes and of the ions with higher charge lowers the levels a, a' etc. Owing to the statistical distribution of these lattice holes and higher charged ions the levels do not have the same height throughout, but as a whole they are all lowered more or less, since with increasing number of such vacant lattice points the direct environment of ions adjacent to the hole becomes increasingly more symmetrical and their average height above the $3d$ band is therefore lowered continually. The lowest levels give the largest contributions to mechanism (3). Actually we find that the activation energy as derived from the temperature coefficient of the conductivity of Cu_2O decreases from 0·72 volts to 0·13 volts with increasing oxygen content(23). In the case of CuJ(24) a sufficient excess of iodine (corresponding to $Cu_{0\cdot 996}J$) leads to a negative temperature coefficient, indicating that in that case the lowest levels a, a' etc. do not rise any more above the highest members of the lattice $3d$ band.

Photoconductivity occurs with Cu_2O and CuJ, not with NiO (independently of deviations from stoichiometry). With the aid of the models given above we may make the tentative hypothesis that photoconductivity, for equal relative positions of the bands with respect to the potential barriers, will be much greater in the case of figure 2 than of figure 1. This can be seen in the following way. Transitions from the lattice $3d$ band into the levels a, a' etc. need not be considered, since as optical transitions they are not allowed. Transitions (1) and (2) are permitted; both transitions can be deduced from the spectral distribution of photoconductivity in the case of Cu_2O with an excess of oxygen, a normal band with a maximum of 630 mμ. and a band connected with the oxygen excess at about 1700 mμ.(25). In the case of a substance with a completely filled $3d$ band a photoelectrically released electron, moving through the lattice under the influence of an applied field, for instance from a Cu^+ ion adjacent to a vacant lattice point, can only fall back to a lower level when it encounters an electronic hole. In the case of NiO, however, the wandering electron can fall back at any time to the $3d$ band, since sufficient empty electronic states are available. Also in this $3d$ band the additional electron can travel further through the lattice, until it reaches an electronic hole (Ni^{3+} ion), but in this band its mobility is considerably smaller than in the $4s$ band, owing to the higher potential barriers to be penetrated; hence only the electrons in the $4s$ band should make a practical contribution to the photoconduction. As a consequence of the much smaller average path length the photoconductivity in NiO will then be correspondingly smaller for otherwise equal conditions.

Another possibility, explaining the photoconductivity of these substances with completely filled bands, which cannot wholly be excluded, is suggested by our remark in § 2 that in CuJ the electron deficit at the lattice holes is perhaps not present at the copper ions (producing Cu^{2+}), but at the J^- ions (thus converted into J atoms). If the latter corresponds to the actual state of affairs for CuJ, the transition of an electron from the Cu^+ $3d$ band into the $5p$ level of those J atoms takes the place of transition (3), and this is permitted as an optical transition. In that case photoconduction can be explained as conduction in the Cu^+ $3d$ band as a consequence of optically released electrons according to the (modified) transition (3). This might be the mechanism for all these substances, if it could be proved to be a general rule that with cations with a complete electronic group or subgroup the electron deficit at the lattice holes is preferably located at the anions. For this a more careful calculation of the electronic levels, which must be reserved to the future, would be necessary.

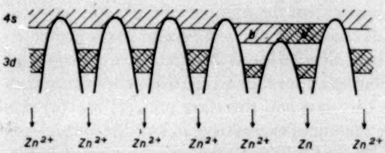


Figure 3. Schematic representation of the $3d$ and $4s$ band in a substance like ZnO, containing a small amount of Zn in excess. Section through a row of Zn^{2+} ions touching a lattice hole due to an absent oxygen ion.

For sake of completeness we also give, figure 3, the situation of the levels for ZnO containing a small amount of metal in excess, on the assumption of vacant oxygen lattice points. Electronic conduction occurs after thermal excitation of an electron from the occupied $4s$ level b' (Zn atom adjacent to a vacant oxygen lattice point) into the $4s$ band, converting a normal lattice ion into Zn^+. Photoconductivity can occur by excitation from $3d$ either into a level b, b' etc. or into the normal $4s$ band.

Finally it should be pointed out that several features of these semiconductors could be understood with the aid of a model using Smekal's structure-sensitive lattice flaws(26). The above picture, however, enables a more complete description of the phenomena and seems preferable in the light of recent results on lattices with vacant lattice points(27, 28) and on the nature of thermal lattice deviations by Wagner and Schottky.*

REFERENCES

(1) Sommerfeld, A. and Bethe, H. *Handbuch der Physik*, **24** (2), 2. Auflage, 368 (1933).
(2) Brillouin, L. Die Quantenstatistik (1931). Berlin: Julius Springer Verlag.
(3) Mott, N. F. and Jones, H. *Theory of the Properties of Metals and Alloys* (1936). Oxford: Clarendon Press.
(4) Wilson, A. H. *Proc. roy. Soc.* A, **133**, 458 (1931); **134**, 277 (1931).
(5) Fowler, R. H. *Proc. roy. Soc.* A, **140**, 505 (1933); **141**, 56 (1933).
(6) Bacher, R. F. and Goudsmit, S. *Atomic Energy States* (1932). McGraw Hill.
(7) Gorter, C. J. Paramagnetische Salze (Diss.). *Arch. Mus. Teyler*, **7**, 183 (1932).
(8) Le Blanc, M. and Sachse, H. *Phys. Z.* **32**, 887 (1931).
(9) Gudden, B. *Ergebn. exakt. Naturw.* **13**, 223 (1934).
(10) Wagner, C. *Z. phys. Chem.* B, **22**, 181 (1933).
(11) Wagner, C. *Phys. Z.* **36**, 721 (1935).
(12) Verwey, E. J. W. and de Boer, J. H. *Rec. Trav. chim. Pays-Bas*, **55**, 531 (1936).
(13) Wagner, C. and Koch, E. *Z. phys. Chem.* B, **32**, 439 (1936).
(14) Schottky, W. *Z. phys. Chem.* B, **29**, 335 (1935).
(15) Jette, E. R. and Foote, F. *J. Chem. Phys.* **1**, 29 (1933).
(16) Klemm, W. and Hass, K. *Z. anorg. Chem.* **219**, 82 (1934).
(17) Dünwald, H. and Wagner, C. *Z. phys. Chem.* B, **22**, 212 (1933).
(18) Schottky, W. and Waibel, F. *Phys. Z.* **36**, 912 (1935).
(19) Schriel, M. *Z. anorg. Chem.* **231**, 313 (1937).
(20) v. Baumbach, H. H., Dünwald, H. and Wagner, C. *Z. phys. Chem.* B, **22**, 226 (1935).
(21) Hund, F. *Phys. Z.* **36**, 728 (1935).
(22) de Boer, J. H. and van Geel, W. Ch. *Physica*, 's Grav., **2**, 286 (1935).
(23) Jusé, W. P. and Kurtschatow, B. W. *Phys. Z. Sowjet*, **2**, 453 (1932).
(24) Bädeker, K. *Ann. Phys.*, Lpz., **29**, 566 (1909).
(25) de Boer, J. H. *Electron Emission and Adsorption Phenomena*, p. 317 (1935). Camb. Univ. Press.
(26) de Boer, J. H. *Chem. Weekbl.* **32**, 106 (1935).
(27) Hägg, G. *Z. Krystallogr.* **91**, 114 (1935).
(28) Verwey, E. J. W. *J. chem. Phys.* **3**, 592 (1935).
(29) de Boer, J. H. *Rec. Trav. chim. Pays-Bas*, **56**, 301 (1937).

* A similar treatment of the colour centres in the alkali halides has been given by de Boer(29).

DISCUSSION OF THE PAPER BY DE BOER AND VERWEY

Reported by N. F. MOTT

with the help of some notes from

R. PEIERLS

CONSIDERABLE surprise was expressed by several speakers that in crystals such as NiO in which the *d*-bands of the metal atoms were incomplete, the potential barriers between the atoms should be high enough to reduce the conductivity by such an enormous factor as 10^{10}. Mr Wilson pointed out that in that case it would hardly be correct to speak of bands at all, but one should think of sharp energy levels, as in the $4f$ shells of salts of the rare earths. This did not seem likely in view of the relatively small distance between nickel lattice points (2·9 A. compared with 2·5 A. for metallic Ni). Prof. Mott stated that in metallic nickel it is known, from experimental data on the specific heat at low temperatures, that the breadth of the *d*-band is quite large, of the order 1 eV.

Prof. Peierls agreed with Dr de Boer that the existence of semi-conductors with incomplete *d*-bands could not be understood merely by considering the low transparency of the potential barrier. This transparency could be perhaps 10^{-2} or 10^{-3} less than for ordinary metal but not 10^{-10}. He suggested that a rather drastic modification of the present electron theory of metals would be necessary in order to take these facts into account. The solution of the problem would probably be as follows: if the transparency of the potential barriers is low, it is quite possible that the electrostatic interaction between the electrons prevents them from moving at all. At low temperatures the majority of the electrons are in their proper places in the ions. The minority which have happened to cross the potential barrier find therefore all the other atoms occupied, and in order to get through the lattice have to spend a long time in ions already occupied by other electrons. This needs a considerable addition of energy and so is extremely improbable at low temperatures.

It appears, therefore, that if the transparency is at all small, the electrostatic interaction would reduce the conductivity still further and thus that at low temperatures the conductivity is proportional to a high power of the initial transparency. No mathematical development of these ideas has however yet been given.

Prof. Peierls made some further remarks about semi-conductors containing impurities. Suppose the impurity is capable of giving off an electron; it is then not sufficient to remove the electron into one of the adjoining lattice ions, in order to make it free for electronic conduction. This is because the impurity is then left in an ionized state and will attract the electron, which therefore moves in the periodic field of the lattice with a Coulomb field superimposed. It is known that in such a field the electron is capable of discrete bound states of negative energy (as in the field of a positive ion). Only if the energy of the electron is still further increased so that it can overcome this attraction and move right away from the impurity centre will it become a conduction electron in the proper sense. This suggests that, even if, as might conceivably happen, an electron would *gain* energy in moving from the impurity atom to an adjacent lattice ion, nevertheless the lowest state of the electron would *always* be a bound state in the neighbourhood of the impurity centre, in which it, so to speak, revolves round the centre, even though it is not definitely attached. Hence a finite activation energy should always be necessary to produce conduction electrons. This conclusion no longer holds when the number of impurity centres becomes large* because then the electron need not overcome the attraction of its "home" centre completely; already at a small distance from it, it will come under the simultaneous attraction of other centres and will thus be released.

From these arguments one may draw the conclusion that one should never find a substance in which a *small* concentration of impurity can produce a conductivity *without* activation energy.

It may be possible to explain on these lines the dependence of activation energy on concentration shown by most semi-conductors.

Similarly it should be true that pure substances of stoichiometric composition should never show a very small number of conduction electrons with zero activation energy. In this connexion it is perhaps significant that one metal with a very small number of conduction electrons, bismuth, shows a correspondingly small effective electron mass. A small mass means a large radius of the orbit and hence the minimum distance at which the centres will interact is correspondingly increased.

Prof. Pohl called the attention of the conference to the behaviour of AgBr, which at room temperature shows electrolytic conductivity, but which is normally an insulator at low temperatures. If it is irradiated with 10^{12} quanta per cm^3 it shows electronic conductivity like a semi-conductor. The state is destroyed by high temperatures and high fields.

---

* I.e. comparable with number of atoms in the lattice.

PART II

CONDUCTION IN ALLOYS

RESISTANCE OF ALLOYS WITH DISORDERED AND ORDERED ARRANGEMENT OF ATOMS

By G. BORELIUS (Stockholm)

§ 1. RESISTANCE CONCENTRATION DIAGRAMS

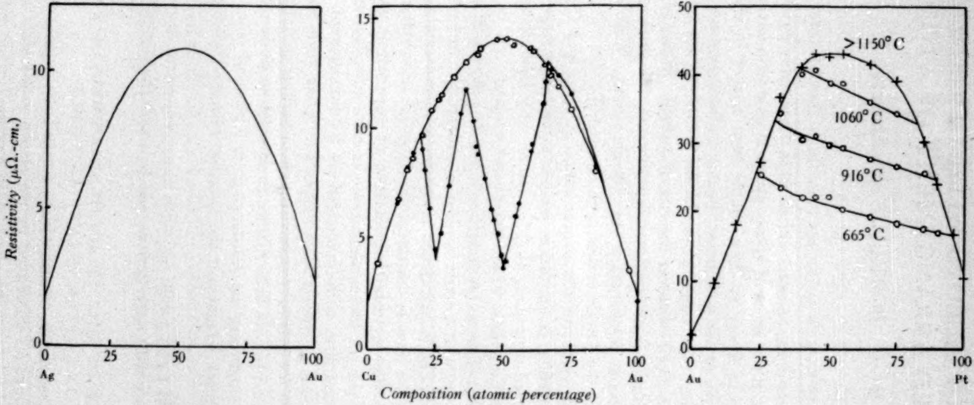
THE general features of the resistance of alloys in the simplest cases is illustrated by the behaviour of the series of binary alloys of gold with silver, copper and platinum shown in figure 1. The simple bent curves in the {resistance, concentration} diagrams, as we now know, belong to homogeneous alloys with a disordered arrangement of the atoms at the lattice points. In the systems Au-Ag this type of curve is obtained whatever the rate of cooling. In the systems Au-Cu and Au-Pt the homogeneous disordered state is stable only at high temperatures and can be preserved at room temperature only by quenching. With slow cooling, ordered states appear in the Au-Cu system with maxima of order and sharp minima of resistance at simple values of the concentration (Cu_3Au and CuAu). In the Au-Pt system the solubility is limited at temperatures below 1150° C., and the resistance curves obtained after quenching from different temperatures are approximately straight lines in the region where two phases co-exist.

Ordered arrangement of atoms (superlattices), and the presence of more than one phase, are thus often very well marked in resistance diagrams. In earlier days most metallographers had very little confidence in resistance measurements as a method in metallography. As the laws of resistance of alloys are now better known, and particularly owing to the increased significance of superlattice formation and segregation processes, the resistance measurements have nowadays an importance in metallography comparable with investigations by microscopes, X rays and thermal analysis. Whereas resistance measurements in recent years have been used by Grube⁽⁴⁾ and others for extensive investigations of various complicated systems of alloys, our measurements have been mainly directed to the study of the resistance and the phenomena influencing the resistance from a physical point of view, and we have in the first place sought out the simplest systems showing the various phenomena.

In the following, §§ 2 and 3 will deal with measurements of disordered homogeneous alloys, §§ 4 to 9 with superlattices, and § 10 with the segregation process.

§ 2. RESISTANCE OF DILUTE SOLID SOLUTIONS OF *b* METALS IN COPPER, SILVER AND GOLD

The shape of the {resistance, concentration} curves of homogeneous alloys without superlattices is above all influenced by the slopes at the sides near the pure metals. It is usual to characterize this slope by the increase ζ in the resistance caused by the addition of one atomic per cent to the pure metal.



(a) (b) (c)

Figure 1. {Resistance, concentration} diagrams for room-temperature. (a) Silver-gold alloys according to measurements of Matthiessen(1). (b) Copper-gold alloys according to Johansson and Linde(2). (c) Gold-platinum alloys according to Johansson and Linde(3).

It was first pointed out by Benedicks(5) in a paper published in the Swedish language that the additional resistance often increases with the distance in the periodic system between the dissolved metal and the solvent. Better known is the work of Norbury(6), who found the horizontal distance in the long-periodic system to be of decisive importance.

Linde(7) has made a very extensive investigation of the increase in resistance of the metals Cu, Ag and Au of the 11th group of the periodic system due to the addition of various metals. The results are especially simple in the case of addition of *b* metals, that is metals from the groups 12 to 15. Figure 2 shows his results from published and unpublished measurements. The square of the difference of group numbers of dissolved metal and solvent is taken as abscissa in these diagrams. The metals of each period give nearly a straight line.

Linde(7) has also pointed out another interesting feature of these additional resistances. They are nearly the same if a certain *b* metal is added to Au or Ag; but on an average only 80 per cent of these values if the same metal is added to Cu. He relates this observation to the fact that the atomic volumes of Au and Ag are 10·3 and 10·2 respectively, whereas the atomic volume of Cu is only 7·1. From this he became interested in the influence of compression on the additional resistance ζ, and he has during recent years obtained a great number of measurements on this subject which are not yet published. The change of resistance of the dilute alloys, measured at pressures up to 3000 kgf./cm^2, is first corrected for the change of volume so as to give the change of specific resistance ρ. Figure 3 shows these changes reduced to 1 kgf./cm^2 for some systems as a function of concentration. The effect of pressure $d\rho/dp$ always gets more negative by addition of *b* metals. This decrease of $d\rho/dp$ for one atomic per cent, divided by the additional resistance ζ per cent, i.e. the quantity $\zeta^{-1}\, d\zeta/dp$, may be looked upon as a pressure coefficient of the additional resistance. As appears from table 1, this quantity is of the same magnitude as the compressibility $V^{-1}\, dV/dp$, as would be expected if the additional resistance contained the atomic volume V as a power not too far from the first as a factor.

Table 1. Pressure coefficients of additional resistance ζ for one atomic per cent of *b* metals in Cu, Ag and Au compared with the coefficient of compressibility of the pure metals. Unpublished measurements by Linde

	Added metals	Copper	Silver	Gold
$\frac{1}{V}\frac{dV}{dp}\cdot 10^6$	—	−0·72	−0·99	−0·58
$\frac{1}{\zeta}\frac{d\zeta}{dp}\cdot 10^6$	Al	−0·4	—	—
	Ga	—	−1·18	−0·68
	Ge	−0·60	—	—
	Sn	−0·66	—	—
	As	−0·45	−0·33	—
	Sb	−0·60	—	—

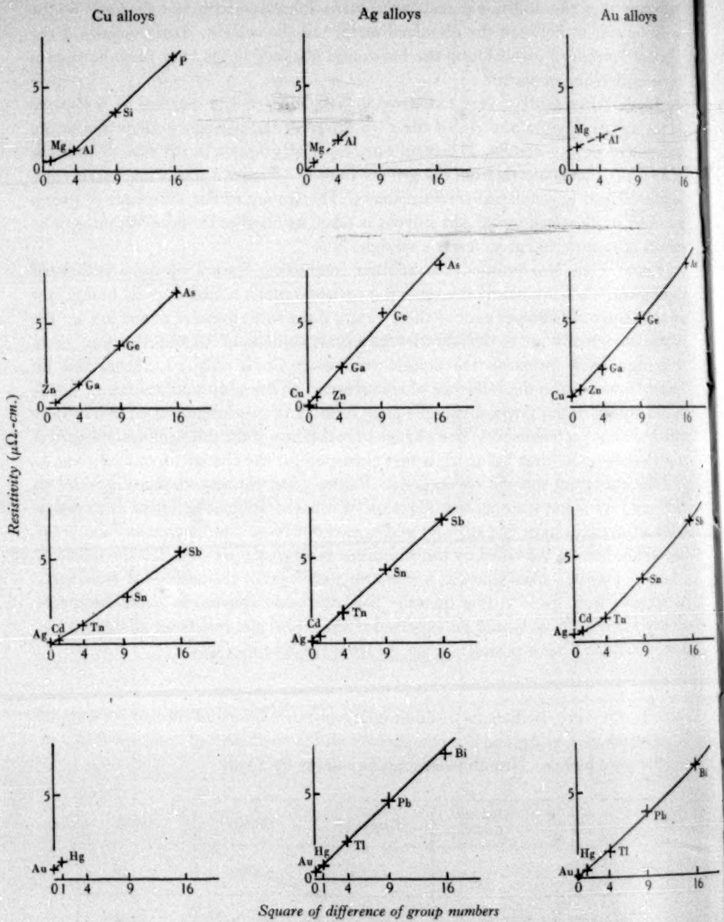


Figure 2. Increase in resistance for 1 atomic per cent of various *b* metals added to copper, silver and gold. (Measurements by Linde.)

For this group of alloys the rule of Matthiessen is also approximately valid. This rule predicts that if the specific resistance ρ of an alloy is written

$$\rho=\rho_0+\rho_T \qquad \text{......(1),}$$

where ρ_0 is the resistance at the absolute zero and ρ_T thus the thermal electric resistance, the addition of foreign atoms to a pure metal increases ρ_0 but has very little influence on ρ_T. In fact Linde has found $d\rho/dT$ to increase slowly with increasing ρ for the dilute alloys of copper, silver and gold with the *b* metals.

The disordered homogeneous alloys of Cu, Ag and Au with each other and with the other *b* metals thus are especially simple in their electric behaviour and have been the first object for theoretical treatment. In the classical electron theory, insuperable difficulties arose already in connexion with the Matthiessen rule. In the general expression for the specific resistance

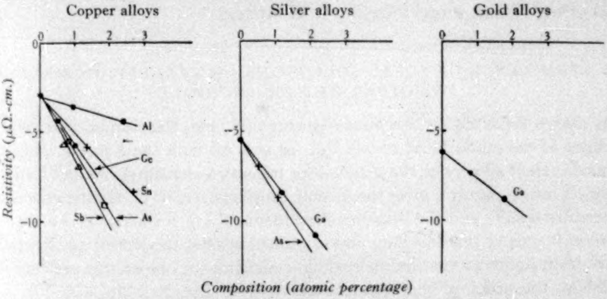


Figure 3. Change of specific resistance for 1 kgf./cm.² due to the addition of *b* metals to copper, silver and gold. (Unpublished measurements by Linde.)

$$\rho=\frac{2m}{e^2}\frac{v}{nl} \qquad \text{......(2),}$$

where *m* and *e* denote mass and charge of an electron, the mean velocity *v* was found to be proportional to the square root of the absolute temperature *T*, and the variation of the number *n* of electrons per cm.³ and their mean free path *l* could not possibly be accounted for in such a way as to give the Matthiessen formula. The modern theory assumes *v* to be large and, to a first approximation, independent of temperature; and the variations of ρ with temperature are mainly due to the variations of *l*. Now $1/l$ is a measure of the scattering of the conducting electrons, and this scattering is a sum of one part, due to thermal agitation, and one due to the disordered arrangement of the foreign atoms.* The scattering of the conducting electrons was first discussed by Bloch(12), who showed that there should be no scattering in a perfect periodic lattice, and the scattering in alloys has been discussed from the standpoint of wave mechanics especially by Nordheim(13) and Mott(14, 15). Mott has managed to give an explanation of the variations of the additional resistance with the group number of the dissolved metal by taking into account the scattering power of the extra field due to the charges of the foreign atoms, those charges being proportional to the differences of the group numbers of the dissolved metal and the solvent.

---

* It might be worth mentioning that this general description of the Matthiessen rule was already given by Höjendahl(8) some years before the appearance of the Sommerfeld theory on the basis of ideas put forward long ago by Wien(9). Though the theory of Höjendahl is now superceded, it should be remembered for its good services in those years when the problems concerning superlattices were first approached. When the Sommerfeld theory appeared(10) it was at once evident and pointed out(11) that this theory was of the general type which could explain the main features of conduction in alloys.

The pressure dependence of the resistance of dilute alloys has been treated theoretically by Lenssen and Michels(16) and Mott(17). Their results, however, do not seem to be in direct agreement with the experimental results of Linde. A re-examination of the assumptions underlying the calculations, with the guidance of the empirical results, might therefore be of interest.

§ 3. RESISTANCE OF SOLID SOLUTIONS OF TRANSITION METALS IN COPPER, SILVER AND GOLD

As shown definitely by the measurements of Linde, the simple rules valid for the alloys of the monovalent metals Cu, Ag and Au with the *b* metals cannot be extended to their alloys with the *a* metals (or transition elements). As an illustration of Linde's results, figure 4 gives the specific resistance ρ at 0° C., the dependence on temperature $d\rho/dT$, and the pressure dependence $d\rho/dp$ for alloys of Au with the transition metals of the first long period plotted against the atomic concentration. We see from figure 4*a* that the increase in resistance for one atomic per cent does not follow the order of the atomic numbers (Ni, Co, Fe, Mn, Cr, Ti); from figure 4*b* we see that the Matthiessen rule which predicts that $d\rho/dT$ should increase slowly with concentration does not hold for these alloys; and from figure 4*c* that the pressure coefficient is of variable size and in most cases positive (it was negative for the alloys with the *b* elements). For Co, Mn and Cr, $(d\zeta/dp)/\zeta$ has the values $-0{\cdot}2$, $+1{\cdot}3$ and $+1{\cdot}1 \times 10^{-6}$ respectively.

In fact, the transition metals influence the resistance of the monovalent metals in a rather individual and varying way, and these variations are of great practical importance in discovering alloys suitable for resistance materials and for pressure measurements. Linde's results have given rise to various new ideas in these directions.

The peculiar influence of the transition metals on the resistance is obviously connected with their strong paramagnetic or ferromagnetic properties. For information about the electric behaviour of these alloys, it is therefore also a matter of importance to study their magnetic properties. In our laboratory Gustafsson(18) is now investigating the paramagnetism of alloys of Cu, Ag and Au with transition metals at temperatures ranging from room temperature to 450° C. The measurements at present include dilute alloys of Cu, Ag and Au with Mn and the systems CuNi and AgPd. His results suggest that a considerable amount of experimental work will be necessary before the paramagnetic alloys are sufficiently classified even from a purely phenomenological point of view. Nevertheless the theory regarding

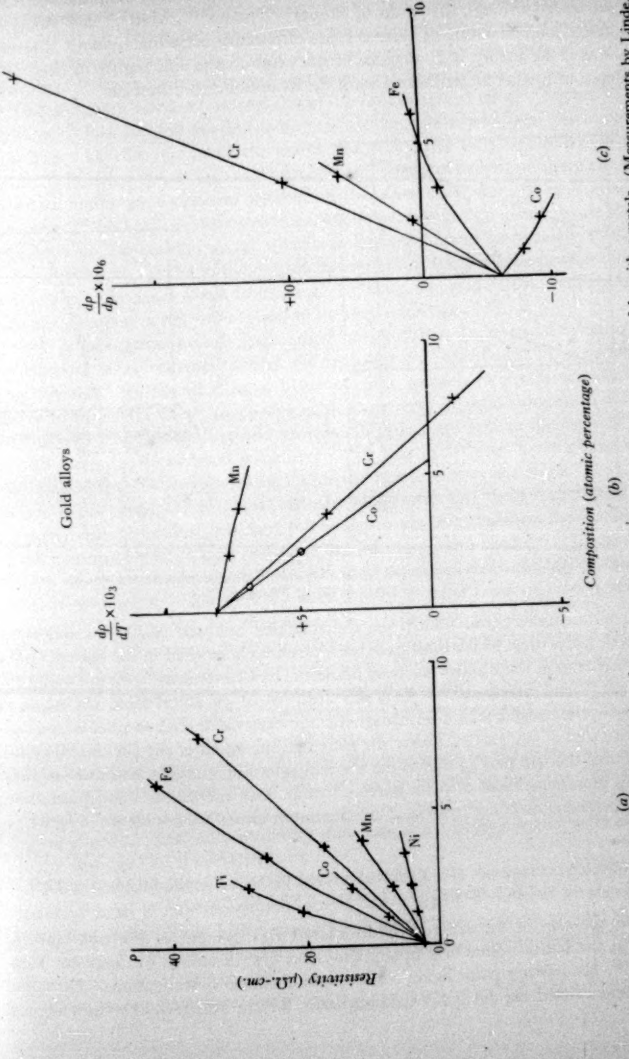
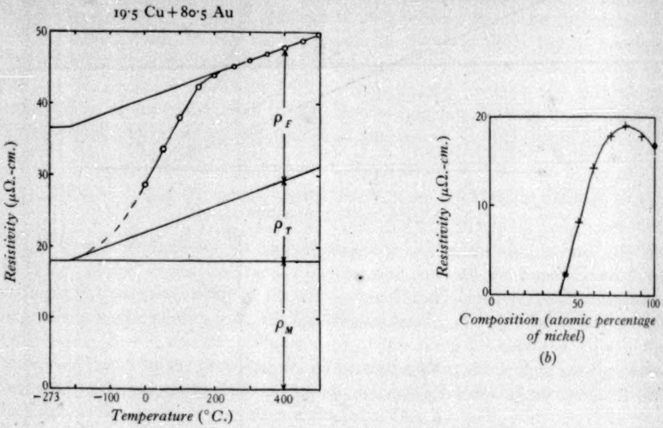


Figure 4. Specific resistance and its dependence on temperature and pressure for dilute alloys of Au with *a* metals. (Measurements by Linde.)

the exchange of electrons between the unfilled electron bands of the transition metals has proceeded through the works of Stoner(19), Slater(20), Mott(21) and others to a qualitative understanding of various types of paramagnetic phenomena. Indeed, it seems as if the theory is in advance of the experiments and highly in need of the guidance of further experimental work for its definite stabilization.



(*b*)

(*a*)

Figure 5. (*a*) Resistance of a ferromagnetic CuNi alloy. (*b*) Ferromagnetic part of resistance of CuNi alloys. (Measurements by Svensson(24).)

Experimentally better known are the relations between resistance and ferromagnetic properties, which both have been extensively studied in the system CuNi. The resistance of these alloys has been measured by Chevenard(22), Krupkowski and de Haas(23) and Svensson(24). As is shown in figure 5*a* taken from the paper of Svensson, the resistance of a ferromagnetic alloy can be described phenomenologically as a sum of one part ρ_M due to the mixed arrangement of the Cu and Ni atoms, one normal thermal part ρ_T due to the thermal agitation of atoms, and one magnetic part ρ_F increasing from 0 to its maximal value with increasing demagnetization. The dependence on concentration of the maximum values of ρ_F is shown in figure 5*b*.

§ 4. DEVELOPMENT OF TRANSFORMATIONS FROM DISORDERED TO ORDERED ATOMIC ARRANGEMENTS

The question of the ordered or disordered arrangement of the two kinds of atoms at the lattice points of a binary alloy was first discussed in detail by Tammann(25), his starting point being results from chemical investigations. He found that there existed certain concentration limits for the resistivity to the chemical action of agencies which attack only one of the components of the alloy. Thus, for example, there were limits at 50 per cent Au for the action of nitric acid on CuAu and AgAu alloys. To explain these limits Tammann found it necessary to assume an ordered arrangement of the atoms and predicted these arrangements from a principle of "best possible mixing" (*bestmögliche Durchmischung*).

This hypothesis led to several X-ray investigations of alloys. Vegard(26) and von Laue(27) had pointed out that an ordered arrangement should give rise to certain extra lines. On the one hand the search for such extra lines in several systems, among them also systems such as AgAu, where Tammann had found sharp chemical resistivity limits, gave negative results; on the other hand, Bain(28) on Cu_3Au and Phragmén(29) on Fe_3Si found extra lines, which were looked upon as support for the hypothesis of Tammann. As at that time there was some uncertainty as to the evidence of X-ray results in the case of incomplete order, it was somewhat difficult to draw the right conclusions from these investigations; also the conclusions drawn from the chemical work were found to be very uncertain(30, 31).

My collaborators and I approached the problem from thermoelectric and conductivity measurements carried out especially by Sedström(32) for a number of alloy systems. We found it most likely that the smooth resistance-concentration curves obtained for these properties in most systems of solid solution indicated a disordered arrangement of atoms, whereas the sharp minima in the cases of compounds were due to ordered structures. With this hypothesis X-ray examinations were started with the results of the resistance measurements as a guide. The examination of the systems PdCu and PdAu by Holgersson and Sedström(33) gave some support to this hypothesis and later full evidence was obtained from the examination of the systems CuAu, CuPd and CuPt by Johansson and Linde(34). In the CuAu system the compounds Cu_3Au and CuAu formed by slow cooling of the solid solutions somewhat below 400° C. were known to exist from an investigation by Kurnakow, Zemczuzny and Zasedatelev(35). Johansson and Linde(34) found that alloys of this system quenched from above 400° C., giving high resistance values on the smooth curve in figure 1*b* first observed by Matthiessen, only gave the ordinary X-ray interferences due to the face-centred cubic lattice, whereas the alloys with concentrations in the neighbourhood of 25 and 50 per cent Au, which were tempered below 400° C. to get small resistance values, showed extra interferences indicating ordered arrangement of the two kinds of atoms on the lattice points. These extra interferences appeared not only at exactly 25 and 50 per cent, but on both sides of these concentration points in wide ranges, at the boundary of which the degree of order could only be a very moderate one. Similar results were obtained for the systems CuPd and CuPt.

These investigations thus showed that the X-ray methods were capable of detecting even a very incomplete order, that a highly disordered arrangement of atoms was, especially at high temperatures, a very frequent case in solid solutions, and that the ordered arrangement appeared only at certain limited ranges of concentration and temperature.

These results have been confirmed and extended by a great many investigations in subsequent years. Theoretical discussions have been especially stimulated by the investigations of the CuAu alloys, for which a recent list of references[2] embraces more than 50 papers, and by the investigations of Bradley and Jay[36] of the FeAl alloys.

§ 5. CONTINUOUS VARIATIONS OF DEGREE OF ORDER

The transformations of alloys from disordered to ordered states differed from the well-known transformations of pure metals and salts into new modifications in so far as it was, for the ordering process, possible to imagine a continuous row of intermediate states between full disorder and full order. It was thus possible that the transformations might proceed wholly or in part homogeneously.

To prove this we followed the transformations by resistance measurements[37] and concluded from the results that the transformation was at least in part continuous. The {resistivity, temperature} diagrams obtained for a highly ordered alloy by increasing the temperature had the general appearance shown in figure 6. The straight lines from *a* to *b* and from *e* to *f* apply to the ordered and the disordered states respectively. In both cases the slope $d\rho/dT$ is approximately that calculated from the Matthiessen rule written in the form

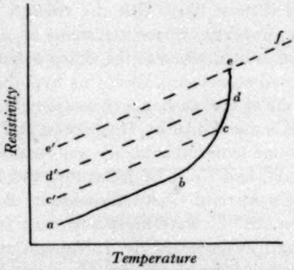


Figure 6. Schematic {resistivity, temperature} diagram of an alloy with superlattice transitions.

$$\frac{d\rho}{dT}=p\left(\frac{d\rho}{dT}\right)_1+q\left(\frac{d\rho}{dT}\right)_2 \qquad \ldots\ldots(3),$$

where $(d\rho/dT)_1$ and $(d\rho/dT)_2$ are the slopes for the pure metals and p and q their fractional parts in the alloy. The curved part of the diagram from *b* to *d* with unusually large values of $d\rho/dT$, represents the continuous variation of structure. That changes of state really occur from *b* to *c* and from *c* to *d* may be proved by quenching the alloy from *b*, *c* and *d* respectively to room temperature. The remaining resistance differences *ac'* and *c'd'* show that a change of state has really taken place. In fact, so far as our present knowledge reaches, values of $d\rho/dT$ much greater than those calculated from the Matthiessen rule always indicate some change either of the magnetic or the structural state. Gorsky[38] at the same time by an X-ray examination of the tetragonality of the AuCu alloy also made the existence of a continuous transformation probable, and, independently of ours, resistivity measurements were carried out by Grube and Weber(38a).

§6. DEFINITIONS OF DEGREE OF DISORDER

A homogeneous solid solution with completely disordered arrangement of the atoms, or a compound with complete order is thermodynamically wholly described by its concentration q, its temperature T, and its pressure p. For the thermodynamical treatment of homogeneous solutions with incomplete order we also need a measure, ξ say, of the degree of disorder. As long as only the thermodynamically stable states are considered, ξ is determined by the values of q, T and p. However, the experimental study of the superlattices shows that frozen and unstable states are easily obtainable as well as the stable ones, and that they are often of the same practical and theoretical importance as the latter. These frozen or unstable states and their measurable physical properties such as energy, entropy, free energy, lattice constants, and resistance, are functions not only of q, T and p but also of ξ as a new independent variable.

Here, in fact, a very great difficulty arises in finding a measure of the degree of disorder that may be both theoretically defined without uncertain assumptions and also put in relation to the various physical properties used for the experimental study of the transition phenomena. The attempts made hitherto to define a suitable degree of disorder (or of order) group themselves along three different theoretical lines.

The first line starts from a discussion of the arrangement of the neighbouring atoms, the discussion having hitherto been limited to the consideration of pairs of atoms. To give an example of the theoretical treatment we may take an alloy of the composition A_3B with a superlattice of the sort found in Cu_3Pd and Cu_3Au. Then in the ordered state a fraction $f_0 = 1/2$ of all pairs of nearest neighbours are of the type AB, and by the disordering process this fraction is decreased to $f_d = 3/8$. A state of incomplete order may therefore be described by the fraction f or better by a degree of disorder

$$\delta = \frac{f_0 - f}{f_0 - f_d} \qquad \ldots\ldots(4),$$

ranging from 0 to 1, or by a degree of order $\sigma = 1 - \delta$. My collaborators and I(37) discussed already in 1928 this way of finding a formal description of the transition phenomena though, for reasons mentioned below, we did not find it very suitable. In recent years, however, Bethe(39) and Peierls(40) have made an extended use of an "order of neighbours" σ, which may be identified with the σ above. Their use of this σ is based on the assumption that the energy of transformation should be proportional to it. I cannot find, however, that there is very much physical support for this assumption; the results of specific heat measurements by Sykes and Jones(41) do not support it. Furthermore the simple use of measures of disorder based on the arrangement of pairs of neighbouring atoms seems to be limited to transitions where the number of nearest neighbours is not altered by the transition process. The 50-per-cent alloys CuPd, CuAu and CuPt in the disordered state are all face-centred with 12 nearest neighbours to each atom, whereas in the ordered state CuPd is body-centred with 8 neighbours, CuAu tetragonal with 8 nearest neighbours and 4 at a somewhat greater distance, and CuPt trigonal with 6 atoms nearest and 6 a little more distant from each atom. Here the use of σ is thus already precluded for purely formal reasons.

The second line starts from the state of full order. If we take as example a 50-per-cent alloy AB, this alloy can be described as a combination of two similar lattices, one containing A atoms, the other B atoms. The fraction p of B atoms in the A lattice (or A atoms in the B lattice) varies from 0 to $\frac{1}{2}$ as the alloy goes from the ordered to the disordered state, and $\alpha = 2p$ or $4p\,(1-p)$, etc., are possible measures of the degree of disorder ranging from 0 to 1. To make such measures quite definite, however, it is necessary to assume the distribution of A and B atoms within each lattice to be statistically disordered, and the truth of this assumption is not quite evident as there might for example be a tendency of the atoms to occur in pairs or small groups in the wrong lattice. Further, it is of course unsatisfactory to extend the idea of different A and B lattices also to the case of great disorder.

A measure of degree of disorder of this kind (called *Fehlordnungsgrad*) was first used by Wagner and Schottky(42) and related to the variations of energy, entropy and resistance in small deviations from full order. Ölander(43) later used it for the theoretical discussion of results of measurements of electrode potentials of alloys at high temperatures. The author(44) made an extended use of a measure of this type for a quantitative treatment of the transition in AuCu. Bragg and Williams(45) used a degree of order of this kind for the treatment of transitions in alloys of the type AB or A_3B and the "long-distance order" of Bethe(39) belongs to the same group of parameters.

In a discussion of the general features of the equilibrium diagrams of systems with superlattices, the author(46) has tried a third line, avoiding parameters based on description of atomic arrangements, and using a purely thermodynamical quantity, the zero-point entropy S_0, as a measure of degree of disorder. For this limited purpose, this parameter is a very suitable one. If the zero-point energy is given as a function of S_0 and the concentration q, certain boundary lines of the equilibrium diagram can be constructed in a simple way. It has not, however, yet been shown whether a quantity like S_0 can be useful also for the treatment of physical properties such as the resistance. This will depend upon whether there exists and can be found some direct theoretical connexion, for instance between zero-point resistance and zero-point entropy.

§ 7. ANTIPHASE REGIONS IN PARTLY ORDERED CRYSTALS

The proposed parameters of degree of disorder are of course single-valued only for homogeneous alloy phases and can only be used for the treatment of states of equilibrium of homogeneous frozen states obtained by quenching, and of the homogeneous metastable states which will be discussed in the next paragraph. As soon, however, as the transitions from disordered to ordered states were followed with X-ray and resistance measurements, my collaborators and I$^{(37)}$ found reasons also for the existence of more complicated transitional states neither fully homogeneous nor in the ordinary sense heterogeneous. If the ordering process starts at, and spreads from, a great many points, the nuclei thus formed will as they meet coalesce if they are in phase with each other, or exist side by side as antiphase regions if they are not. This means that a row or plane of *A* atoms in one region will, as is shown in figure 7 taken from our paper of 1928$^{(37)}$, continue as a row or plane of *B* atoms in the next one.

It was pointed out in this paper that such regions, if they were small enough, must have a great influence on the sharpness of the superlattice lines of X-ray photograms and on the resistance.

This hypothesis of antiphase regions also explains the observation later made by Oshima and Sachs$^{(47)}$ and by Dehlinger and Graf$^{(48)}$ by X-ray examination of single crystals of AuCu, that the tetragonality and the intensities of different superstructure lines do not vary in the same way during the ordering transition. The hypothesis put forth by Oshima and Sachs and especially used by Dehlinger$^{(49)}$ to account for these observations, namely that the tetragonality to a certain extent should be independent of the degree of order, is quite incomprehensible and, at least for the present, unnecessary.

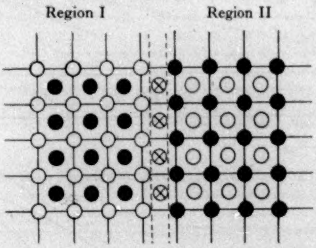


Figure 7. Antiphase regions. ○ *A* atoms, ● *B* atoms, ⊗ *A* or *B* atoms.

In recent years the hypothesis of antiphase regions has indeed obtained very good support in two different ways.

On the one hand Sykes in collaboration with Evans$^{(50)}$ and Jones$^{(41)}$ has made a thorough experimental examination of the transitions in Cu_3Au by measuring lattice constants and intensity of superstructure lines, resistance, and specific heat, and has found it possible to account for a great many details, some even quantitatively, from the assumption of antiphase regions. Figure 8 shows in a schematic way some of their results concerning resistance and energy content, which are interpreted in the following way: As a sample is quenched from above the critical temperature T_0 it remains in the disordered state and resistance and energy varies along the straight lines *a–a*. As the quenched alloy is heated at a rate of about 90° per hour, as shown by the curve *b–b*, the energy begins already at 60° C. to deviate from this line. This decrease in energy content is interpreted as due to the formation of small antiphase regions of an extent of only 6 to 8 atomic diameters. At about 250° C. a new decrease of energy begins owing to an increase of the size of the antiphase regions. At 344° C. this size is about 12 to 14 diameters, being estimated both from the breadth of the superlattice lines and from the energy content. The resistance is not appreciably influenced by the small regions of 6 to 8 diameters but decreases rapidly as the length of the regions exceeds about 10 diameters. This is in qualitative agreement with the fact that the mean free path of the electrons in the ordered alloy is estimated, from modern theory of conduction, at 30 to 40 diameters. The curves *e–e* reached by very slow cooling correspond to regions of about 100 diameters or more and are approximately curves of equilibrium. If an alloy, which is in equilibrium at the point *d′* and thus has large antiphase regions but an incomplete order of atoms, is cooled rapidly enough to preserve the degree of disorder, the resistance follows a straight line *d–d′*. The curve *c–c* finally shows the variation of resistance by slow heating or cooling of a sample with regions of medium size in a temperature

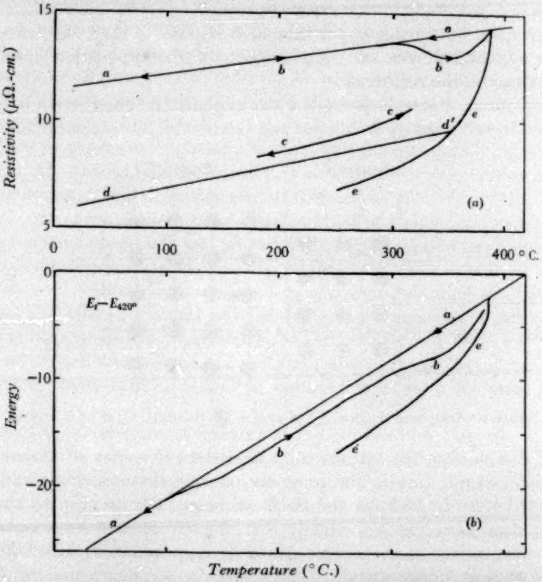


Figure 8. (*a*) Resistivity, (*b*) energy of Cu_3Au. (Measurements by Sykes, Evans and Jones(41, 50)).

range where the regions cannot grow. The bend is due to the variation of degree of disorder inside the regions.

On the other hand Johansson and Linde(2) have found that alloys with compositions around CuAu after suitable heat treatment occur in an ordered state (CuAu II) that can be described as the well-known ordered tetragonal state (CuAu I) found earlier by the same authors split up in antiphase regions of a fixed length. This structure, being periodic, can be directly established by X-ray examinations. At 50 per cent Au the length of each region is, as shown in figure 9, 10 atomic distances, but it increases at both sides in the concentration diagram. As to the theory of electric resistance, it is interesting to notice that these periodic antiphase displacements do not, like the accidental ones of the same mean distances, increase the resistance. Alloys with the structures CuAu I and CuAu II lie in figure 1*b* on the same resistance curve.

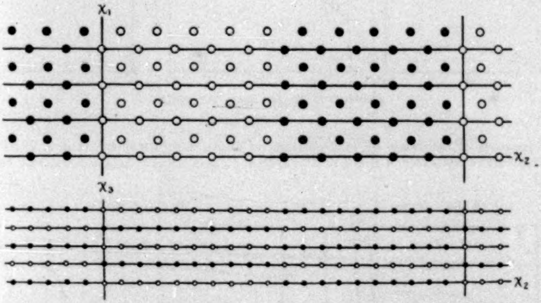


Figure 9. Structure of CuAu II according to Johansson and Linde(2).

§ 8. DISORDERING BY MECHANICAL TREATMENT

The superstructure of an alloy can be destroyed not only by heating but also by cold working. This was made probable by X-ray investigations of Dehlinger and Graf(48) on CuAu and of Schäfer(51) on FeAl and is shown very convincingly by Dahl(52) by X-ray investigations together with resistance measurements on Cu_3Au. Fig. 10*a* shows the increase in resistance for an annealed Cu_3Au alloy as a function of the decrease of section area by cold workings. Figures 10*b* and 10*c* show corresponding curves for two Cu-Pt alloys obtained by Linde in connexion with an unpublished re-examination of the CuPt system. This effect might be explained by the formation of antiphase regions by the cold working.

§ 9. HYSTERESIS BETWEEN THE ORDERING AND DISORDERING TRANSITIONS

As the transitions between ordered and disordered states were first followed in both directions by resistance measurements, in many cases a well-marked hysteresis loop in the {resistivity, temperature} diagram was found. Figure 11 gives two examples from our first investigation[(37)], showing the behaviour of quenched alloys during slow heating and subsequent slow cooling. In heating an ordering process is observed to begin at the temperatures marked as T_1 and by further heating full disorder is reached at the temperatures T_3. In the subsequent cooling the alloy remains in the disordered state far below T_3 until about a temperature T_2 when the speed of the ordering process increases rapidly within a range of a few degrees. The disordered alloy could be held for many hours at temperatures between T_3 and T_2 (not too near T_2) without showing any signs of beginning a transition into order. Thus we found a well-established hysteresis in CuAu and CuPd, whereas we estimated the transitions of Cu_3Pd to be without hysteresis. The recent very thorough examinations Cu_3Au by Sykes and Evans[(50)] have shown that there is also in the case of Cu_3Au a well-marked hysteresis though only extending over a few degrees on the temperature scale.

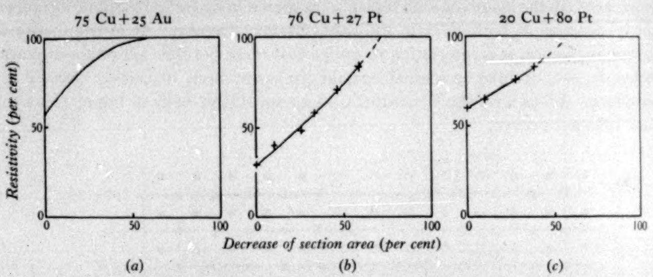


Figure 10. Increase of resistance by cold-working of alloys with super-structures. Resistance as a percentage of the resistance of the disordered state. (Unpublished measurements by Dahl[(52)] and Linde.)

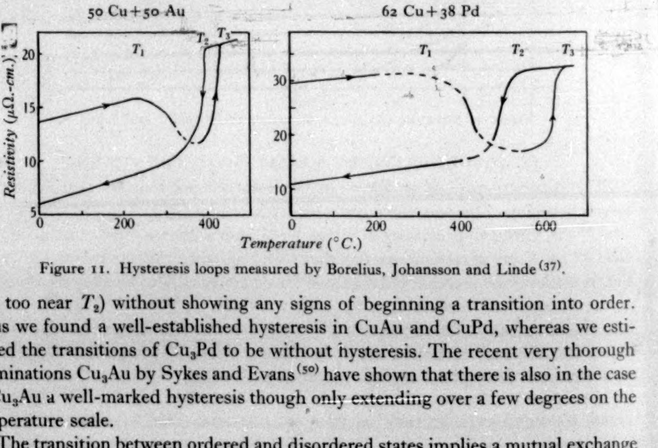


Figure 11. Hysteresis loops measured by Borelius, Johansson and Linde[(37)].

The transition between ordered and disordered states implies a mutual exchange of places of atoms two by two. It is clear that a slowness of this exchange will, by rapid cooling or heating, cause the state of the alloy to lag behind its stable state and thus gives rise to a hysteresis loop. This type of hysteresis has been mathematically treated by Bragg and Williams$^{(45)}$. It will be expected to be less pronounced the higher the temperature. As, however, the hysteresis found by our measurements was very pronounced also at temperatures at which we must expect a lively exchange of places of the atoms, we found it necessary to ascribe the hysteresis to thermodynamically metastable states and it was shown$^{(44, 45)}$ that such metastable states were to be expected for certain types of the free energy F as a function of temperature T and degree of disorder ξ shown in figure 12. Point *a* represents a metastable state in heating, and point *b* in cooling, *c* represents stable states. Even where the free energy is not of this type a certain hysteresis could be expected thermodynamically as a result of internal stresses. There has been some doubt$^{(45)}$ whether such theoretical metastable states could really account for the hysteresis observed but, so far as I can see, no better explanation has as yet been given.

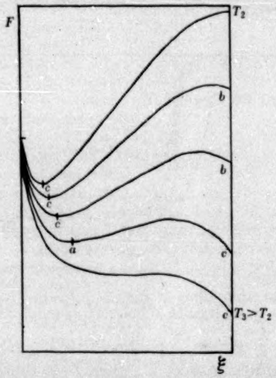


Figure 12. Isothermals of free energy F as a function of degree of disorder ξ according to Borelius$^{(44)}$.

§ 10. HYSTERESIS AT THE SEGREGATION PROCESS

The idea of relative minima of free energy as a cause of hysteresis of the superlattice transitions led to a search for similar phenomena in connexion with the segregation of a homogeneous alloy into two phases, and in fact resistance measurements of the system AuPt have given a very good support for this idea. As was found by Johansson and Linde$^{(3)}$, AuPt alloys of all concentrations can be brought into a homogeneous solid state by heating to sufficiently high temperatures. If these homogeneous alloys are quenched to say 800° C., where there is in the stable state a gap in the solubility from 25 to 90 atomic per cent Pt, the free energy of the homogeneous alloys obtained by quenching will, as was calculated by the author$^{(53)}$ from the equilibrium diagram, depend on the concentration approximately in a way shown in the upper section of figure 13. From *a* to *d* the homogeneous alloys are unstable. From *a* to *b* and from *c* to *d* where the curve is bent upwards the segregation that has to begin as a small increase of the Pt concentration in certain regions and a small decrease in the neighbouring ones will first cause an increase in the free energy and thus to a certain extent be prevented. The resistance measurements of Johansson and Hagsten(54) on an alloy with 30 atomic per cent Pt, and unpublished measurements of Wictorin on alloys from 25 to 50 per cent Pt agree very well with these expectations. The lower section of figure 13 shows the decrease in resistance, here a measure of the segregation, for alloys first quenched in the homogeneous state from high temperatures to 800° C., then held there for τ min. and finally quenched to room temperature. The curves for small values of τ show points of inflexion at a concentration *ii* corresponding to the calculated inflexion in the free-energy diagram. Similar results are obtained at 900° and 700° C. When the free-energy curve is strongly bent upwards, in spite of the high temperatures and the probable high mobility of the atoms, the segregation is still a very slow one. The reverse process, the reconstitution of an homogeneous alloy, presents no such obstacles.

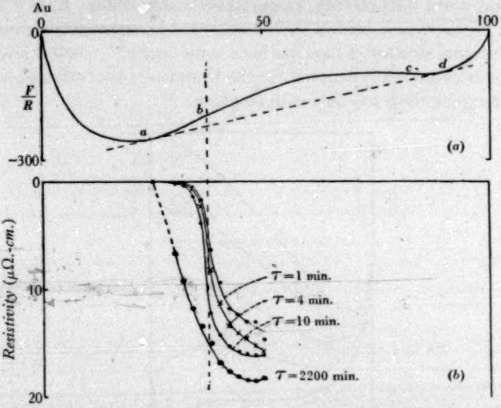


Figure 13. (*a*) Free energy of AuPt alloys at 800° C., calculated from the equilibrium diagram. (*b*) Decrease in resistance by segregation at 800°. (Unpublished measurements by Wictorin.)

REFERENCES

(1) Matthiessen, A. *Ann. Phys.*, Lpz., **110**, 190 (1860).
(2) Johansson, C. H. and Linde, J. O. *Ann. Phys.*, Lpz., **25**, 1 (1936).
(3) Johansson, C. H. and Linde, J. O. *Ann. Phys.*, Lpz., **5**, 762 (1930).
(4) Grube, G. and collaborators. Twenty-two papers mostly in *Z. Elektrochem.* 1929–37.
(5) Benedicks, C. *Jernkontor. Ann.* p. 35 (1916).
(6) Norbury, A. L. *Trans. Faraday Soc.* **16**, 570 (1927).
(7) Linde, J. O. *Ann. Phys.*, Lpz., **10**, 52 (1931); **14**, 353 (1932); **15**, 219 (1932); *Metallwirtschaft.* **12**, 173 (1933).

(8) Höjendahl, K. *Phil. Mag.* **48**, 349 (1924).
(9) Wien, W. *S.B. Akad. Wiss. Wien*, p. 84 (1913).
(10) Sommerfeld, A. *Z. Phys.* **47**, 1 and 43 (1928).
(11) Borelius, G. *Ann. Phys.*, Lpz., **84**, 907 (1927).
(12) Bloch, F. *Z. Phys.* **52**, 555 (1929); **59**, 208 (1930).
(13) Nordheim, L. *Ann. Phys.*, Lpz., **9**, 607 (1931).
(14) Mott, N. F. *Proc. Camb. Phil. Soc.* **32**, 281 (1936).
(15) Mott, N. F. and Jones, H. *Properties of Metals*, p. 286ff. (1936). Oxford.
(16) Lenssen, M. H. and Michels, A. *Physica*, 's Grav., **2**, 1091 (1935).
(17) Mott, N. F. *Proc. phys. Soc.* **46**, 680 (1934).
(18) Gustafsson, G. *Ann. Phys.*, Lpz., **25**, 545 (1936); **28**, 121 (1937).
(19) Stoner, E. C. *Proc. roy. Soc.* **152**, 672 (1935); **154**, 656 (1936).
(20) Slater, J. C. *Phys. Rev.* **49**, 537 and 931 (1936).
(21) Mott, N. F. *Proc. phys. Soc.* **47**, 571 (1935); *Proc. roy. Soc.* **153**, 699 (1936) and **156**, 368 (1936).
(22) Chevenard, P. *J. Inst. Met.* **36**, 39 (1926).
(23) Krupkowski, A. and de Haas, W. J. *Commun. phys. Lab. Univ. Leiden*, **194**, 1 (1928).
(24) Svensson, B. *Ann. Phys.*, Lpz., **25**, 263 (1936).
(25) Tammann, G. *Z. anorg. Chem.* **107**, 1 (1929).
(26) Vegard, L. and Schjelderup, H. *Phys. Z.* **18**, 93 (1917).
(27) v. Laue, M. *Ann. Phys.*, Lpz., **56**, 497 (1918).
(28) Bain, E. *Trans. Amer. Inst. min. (metall.) Met. Engrs*, **68**, 625 (1923).
(29) Phragmén, G. *Stahl. u. Eisen*, no. 9 (1925).
(30) Masing, G. *Z. anorg. Chem.* **118**, 293 (1921).
(31) Borelius, G. *Ann. Phys.*, Lpz., **74**, 216 (1924).
(32) Sedström, E. Dissertation Lund (1924).
(33) Holgersson, S. and Sedström, E. *Ann. Phys.*, Lpz., **75**, 143 (1924).
(34) Johansson, C. H. and Linde, J. O. *Ann. Phys.*, Lpz., **78**, 439 (1925); **82**, 449 (1927).
(35) Kurnakow, N., Zemczuzny, S. and Zasedatelev. *J. Inst. Met.* **155**, 305 (1916).
(36) Bradley, A. J. and Jay, A. H. *Proc. roy. Soc.* **136**, 210 (1932).
(37) Borelius, G., Johansson, C. H. and Linde, J. O. *Ann. Phys.*, Lpz., **86**, 291 (1928).
(38) Gorsky, W. *Z. Phys.* **50**, 64 (1928).
(38*a*) Weber, W. Dissertation Stuttgart (1927).
(39) Bethe, H. *Proc. roy. Soc.* **150**, 552 (1935).
(40) Peierls, R. *Proc. roy. Soc.* **154**, 207 (1936).
(41) Sykes, G. and Jones, F. W. *Proc. roy. Soc.* **157**, 213 (1936).
(42) Wagner, C. and Schottky, W. *Z. phys. Chem.* **11** (B), 163 (1930).
(43) Ölander, A. *Z. phys. Chem.* **165** (A), 65 (1933).
(44) Borelius, G. *Ann. Phys.*, Lpz., **20**, 57 (1934).
(45) Bragg, W. L. and Williams, E. J. *Proc. roy. Soc.* **145**, 699 (1934); **152**, 540 (1935).
(46) Borelius, G. *Ann. Phys.*, Lpz., **24**, 489 (1935).
(47) Oshima, K. and Sachs, G. *Ann. Phys.*, Lpz., **14**, 481 (1932).
(48) Dehlinger, U. and Graf, L. *Z. Phys.* **64**, 359 (1930).
(49) Dehlinger, U. *Z. Phys.* **64**, 359 (1930); **74**, 267 (1932); **83**, 832 (1933).
(50) Sykes, C. and Evans, H. *J. Inst. Met.* **58**, 255 (1936).
(51) Schäfer, K. *Naturwissenschaften*, **10**, 207 (1933).
(52) Dahl, O. *Z. Metallk.* **28**, 133 (1936).
(53) Borelius, G. *Ann. Phys.*, Lpz., **28**, 507 (1937).
(54) Johansson, C. H. and Hagsten, O. *Ann. Phys.*, Lpz., **28**, 520 (1937).

A STUDY OF THE ORDER-DISORDER TRANSFORMATION

By W. L. BRAGG, C. SYKES and A. J. BRADLEY

§1. INTRODUCTION

The present account is a summary of a series of related researches into the order-disorder transformation, carried out at Manchester University and in the research laboratory of Messrs Metropolitan Vickers. Our researches have been planned to take their places in a concerted scheme, and it is hoped that this general summary and the list of papers at the end of this article will be a useful indication of their scope. Similar researches have been in progress in other laboratories. Though this account is restricted to the researches at Manchester, it is published with full acknowledgement of the work carried out elsewhere, particularly by Borelius, Dehlinger, Johannson and Linde, and others.

The order-disorder transformation has been followed by means of X-rays by Bradley and his coworkers. The theory of the transformation has been developed by Bragg and Williams, by Bethe, and by Peierls. The measurements of the changes in internal energy, in conductivity, and in some cases in magnetic properties, have been made by Sykes. A résumé of the programme of work in hand is given at the end of the article.

§2. THE GENERAL NATURE OF THE ORDER-DISORDER TRANSFORMATION

Examples of the order-disorder transformation and of its effect upon the physical properties of alloys are to be found in Bradley and Jay(1, 2), Bradley and Rodgers(3) and Sykes and Evans(4). All transformations as yet observed in binary alloys occur when the proportions of the constituents are approximately in the ratio 1 : 1 or 1 : 3. In the disordered state observed at high temperatures the atoms A and B of the two metals are arranged at random amongst the position of a pattern such as the face-centred at body-centred cubic lattice. In the ordered state at low temperatures atoms of each kind segregate into regular positions. For instance, in the classic case of Cu_3Au gold and copper atoms are distributed at random amongst positions of a face-centred cubic lattice when the temperature is high, whereas gold atoms occupy cube corners and copper atoms face centres in a regular way at low temperatures. There are other more complex cases when more than two types of atoms are involved, such as the Heusler alloy Cu_2MnAl or the alloy Fe_2NiAl. In the latter, corners of cubes are occupied by Fe and Ni in a random way, centres by Fe and Al in a random way. The ordering process is thus restricted to a distinction between Ni and Al, but does not extend to a distinction between either of these and iron. We may compare the ordering phenomenon to the passage of the alloy through two successive processes of crystallization on cooling. In the first process the liquid becomes a crystalline solid. Atoms take up positions at regular sites, for instance those of a face-centred lattice, but there is as yet no distinction between atoms of either kind A and B. As the temperature falls still farther, a second crystallization within the solid crystalline lattice takes place, by the segregation of the atoms into regular positions. In both cases there is an increase of regularity, implying a decrease in the entropy and a decrease in the internal energy. This alteration of internal energy is the latent heat of fusion in the first case, and something analogous to a latent heat in the second case. There is an important difference between the two cases. At the freezing-point the substance passes over completely from the random arrangement of the liquid to the ordered arrangement of the solid. Intermediate states between liquid and solid would have an extremely high internal energy, and therefore the substance does not pass through them. Bernal has illustrated this feature by a striking two-dimensional model (19). If a number of non-overlapping circles are drawn on a sheet of paper, they must either be packed in an orderly way, or there must be numerous gross misfits of contact; a series of slight misfits is geometrically impossible, unless we permit circles to overlap which implies large internal energy of strain. On the other hand, intermediate stages between complete order and disorder involve no excessive values of the internal energy. When crystallization of the second kind sets in, it is at first one of partial order and theoretically does not become one of complete order until the absolute zero is reached. Actually it is nearly complete at 100 or 200° C. below the temperature at which it starts. The ordering goes on over this whole range, and latent energy is evolved in cooling or absorbed on heating. Thus what corresponds to the latent heat of the first crystallization is spread out into an abnormally high specific heat over a wide temperature range in the second crystallization.

Although the completion of ordering is so gradual, it sets in at a sharply marked *critical temperature*. We can see that this must be the case by considering the reverse process of heating the ordered alloy. At first the passage of each atom from an ordered to a disordered position involves a certain amount of work V_0 required to thrust it out of relation to its ordered neighbours. As temperature increases there is an increase in the energy kT which determines the number of atoms in the state of higher energy, and at the same time there is a decrease in the energy V required to move an atom to a position of disorder, because each atom has more neighbours already disordered. These two variations so interact that there is finally a catastrophe, or complete breakdown of general order, at the critical temperature. The critical temperature corresponds to the Curie point of a ferromagnetic. In the general case, there is first a jump from a state of disorder to one of partial order with latent heat at the critical temperature and then a gradual increase of order as temperature falls. In special cases the alloy may pass continuously through all intermediate stages of order; the critical temperature is marked by a peak in the specific heat, but no latent heat is involved or absorbed.

So far it has been assumed that the alloys are in thermodynamical equilibrium at each temperature. Actually at temperatures below 200 or 300° C. the atoms interchange position very sluggishly. The influence of the rate of relaxation upon the degree of order must be studied. It is possible to freeze some alloys in the disordered state by quenching (we may compare them to supercooled liquids). It will be seen below, however, that the slowness with which they devitrify back into an ordered scheme is not so much due to sluggishness of atomic interchange as to the establishment in them of numerous nuclei of order which are out of phase with each other.

§ 3. THE THEORY OF THE DEPENDENCE OF ORDER UPON TEMPERATURE

The order-disorder change provides a very interesting exercise for thermodynamic theory. It may be considered in two ways. At a given temperature there is a partition of the atoms between ordered and disordered positions depending upon the amount of energy V required to move an atom from the ordered to the disordered position. A further assumption as to the dependence of this energy upon the existing degree of order establishes an equation for equilibrium at that temperature, and so leads to the general relation between temperature and degree of order. Alternatively an expression for the free energy F of the alloy in any given state of order may be formed. Since $F=U-TS$, an assumption as to the dependence of the internal energy U upon the degree of order must be made, based on the mutual potential energy of like and unlike neighbours A and B. The entropy S can be calculated from the number of complexions of the given state of order. The condition for equilibrium is then expressed as $\partial S/\partial\sigma=0$, where σ is a parameter defining the degree of order. The two methods are of course equivalent and lead to the same equation. The latter method has been used by Borelius and by Dehlinger, the former by Bragg and Williams. The particular interest of the order-disorder change is that the entropy S can be calculated by first principles, since it simply depends upon the number of permutations of the atoms A and B. In this respect it is so much simpler than the change between liquid and solid, or between one allotropic modification and another.

Bragg and Williams(5) calculate the degree of order as a function of temperature, for cases where the atoms are in numerical ratios 1 : 1 and 1 : 3. The energy V is supposed to be proportional to the average degree of order of the whole surrounding structure.

Bethe(10) carries out the far more complex calculation of the dependence of order on temperature on the assumption that the mutual potential energy depends upon nearest neighbours alone. When this assumption is made the new and highly interesting feature of local order appears. If it be assumed that the ordering energy V depends on the general scheme of order of the whole structure, then V becomes zero with the vanishing of long-distance order at the critical temperature. If, on the other hand, V depends upon nearest neighbours only as Bethe assumes, we find that, although long-distance order vanishes at the critical temperature, nuclei of local order persist. Schemes of order over restricted volumes are constantly appearing and being broken up, because it is always more likely that the nearest neighbour to an *A* atom will be a *B* atom rather than an *A* atom. Experiment as will be shown below indicates that Bethe's assumption is in closer accord with fact. Local order still has the effect of reducing the entropy and increasing the specific heat even above the critical temperature.

Bragg and Williams(11, 12) contrast the predictions based on their earlier hypothesis and on that of Bethe with the results of Syke's experiment (see below), and the theoretical treatment is amplified. Peierls(13) extends Bethe's treatment to the case of superlattices such as Cu_3Au with a 3 : 1 ratio between the two types of atom. Bethe has confined himself to the case of the ratio 1 : 1. Cu_3Au has been experimentally investigated rather completely, and comparisons between theory and experiment can be made. Neither the assumptions of Bethe nor of Bragg and Williams give a close agreement with the observed energy-temperature curve, but there is sufficient correspondence to prove that theory is on the right lines.

§4. MEASUREMENTS OF ENERGY CHANGES DUE TO THE FORMATION OF THE SUPERLATTICE

The progressive disappearance of superlattice order as temperature is increased is marked by an abnormally high specific heat due to the energy required to transfer atoms into positions of disorder, and by latent heat at the critical temperature where the long-distance order is finally destroyed. In special cases, there is no latent heat because the alloy passes through all stages of order. Above the critical temperature the specific heat should still be slightly above the normal value* due to local order. The measurement of the specific heat for the purpose of testing the theory requires accurate determinations over temperature intervals of a few degrees. Apparatus involving a new principle has been evolved for this purpose by Sykes(7, 16) and has proved to be very successful. The temperature of an outer massive metallic container is raised at a regular rate by a heating coil. The specimen inside the container is also warmed electrically by a measured energy input, which is so controlled that the temperatures of the specimen and container remain closely the same. The apparatus is evacuated. Corrections can be made for the very small heat losses or gains. Difference of temperature between specimen and container can be measured by a thermo-element very exactly indeed since it is so small, and the rate of rise of temperature of the container is accurately known since it can be measured over long time intervals. Hence the data for highly accurate specific heat determinations over short temperature ranges are available.

The features prophesied by theory are all present. The alloys show abnormally high specific heats rising to a maximum just below the critical temperature. The alloy Cu_3Au displays latent heat at the critical temperature, but β brass (CuZn) has none. Above the critical temperature the specific heat is slightly higher than a normal value for pure metals.

---

* There is no direct way of measuring the "normal" specific heat above the critical temperatures, but it can be inferred from the specific heat at low temperatures or the behaviour of alloys of other compositions.

§ 5. TIME OF RELAXATION

An alloy at a given temperature not initially in the state of order characteristic of that temperature will relax towards it at a rate dependent upon the frequency with which atoms interchange their positions. The equation for the time of relaxation τ should have the form

$$\tau = Ae^{W/kT},$$

where A is a constant (of the order 10^{-9} to 10^{-12}) and W measures the energy barrier which has to be surmounted for interchange to take place. The above assumes that we are dealing with a simple case of an alloy in which a general scheme of order is established, but where the number of atoms in ordered positions is not in correspondence with equilibrium. Experiment shows that the actual state of affairs is not so simple (Sykes(14)). It is possible to obtain Cu_3Au at room temperature in a state which is apparently one of disorder as judged by its electrical resistance, by quenching it from above the critical temperature. Measurements made on the relaxation of the alloy back to the equilibrium state cannot be explained by a simple law of the type $\tau = Ae^{W/kT}$. Further, it is known that copper and gold diffuse into each other quite rapidly at 200–250° C., whereas the critical temperature is 391° C. If diffusion takes place at 250° C., atomic interchange at 391° C. should be so extremely rapid that no quenching could be fast enough to preserve the disordered state. Sykes has explained the discrepancy as being due to the formation of antiphase nuclei. Ordering in Cu_3Au takes place by a segregation of the gold atoms at points of one of the four interpenetrating simple cubic lattices which build up its face-centred lattice. All four simple lattices are equivalent, and nuclei of order may start according to any one of four schemes. If numerous nuclei start and grow till they meet the interfaces of nuclei with different schemes (antiphase nuclei), there must be disordered regions, since the atoms at and near the interfaces cannot conform to both schemes. This appears to be the state of affairs in an alloy "frozen" in disorder. The conglomerate of antiphase regions is very stable. Sykes has proved their existence and measured their size by means of X rays. Their effect on internal energy and on electrical resistance has been measured(15). The quenched alloy with its numerous antiphase nuclei has an electrical resistance at room temperature which fits upon an extrapolation of the resistance curve of the disordered alloy above the critical temperature. It behaves electrically, in other words, as if it were completely disordered. On the other hand, the internal energy is lower than would be expected for complete disorder, showing that some approach to ordering has taken place.

Sykes has further shown that if the alloy is soaked for 48 hours at a temperature only a degree or so below the critical temperature, the antiphase nuclei coalesce into large regions over which the scheme of order is consistent. Once the alloy has been brought into this state it remains in equilibrium as its temperature is raised or lowered (even at fast rates), always provided the critical temperature is not exceeded. At low temperatures the alloy in this state has an electrical resistance like that of a pure metal tending towards zero as the absolute temperature is approached.

It is easy to quench Cu_3Au with its four schemes of order into a state resembling one of complete disorder. On the other hand, it is impossible to quench CuZn in the disordered state. This is probably due to the fact that the latter alloy has only two alternative schemes of order (cube corners or centres for Cu or Zn). Four types of antiphase nuclei can form a stable froth (the boundaries behave as if they had surface tension), but two types cannot do so. Hence CuZn always breaks down into large regions which have a consistent ordered scheme.

§6. THE INFLUENCE OF ORDER ON MAGNETIC PROPERTIES

The alloy Fe_3Al shows peculiar magnetic effects, having two Curie points. Sykes has shown (8) that this phenomenon is due to the ordering process. As the alloy in the disordered state cools from a high temperature it reaches a Curie point and becomes ferromagnetic. At a slightly lower temperature order sets in. This critical temperature is below the Curie point for the disordered state but above that for the ordered state, hence the alloy loses its ferromagnetism. On cooling further it reaches the Curie point for the ordered state and becomes ferromagnetic again. Very interesting effects are produced by varying rates of cooling and heating.

Bradley has studied the effect of order on the ferromagnetism of the Heusler Alloys (3).

§7. WORK AT PRESENT IN PROGRESS OR ABOUT TO BE PUBLISHED

Measurements have been made of the energy of ordering in βCuZn alloys which depart from the equiatomic ratio. These measurements are in satisfactory accord with theory (17). The existence of a superlattice in β brass, hitherto only inferred from its behaviour, has been definitely proved by Sykes and Jones (16). Powder photographs have been taken with ZnK_α radiation. The proximity of this wave-length to the absorption edges of Cu and Zn introduces an enhanced difference of scattering power which causes the lines in the powder photograph for which $(h+k+l)$ is uneven to appear.

Several alloys which show ordering with a 1 : 1 atomic ratio of constituents are being studied thermally, electrically, and by X rays, in order to check theory with more experimental measurements (AgCd, AgZn, MgCd, etc.).

The alloy Cu_3Pd, which it was hoped would behave like Cu_3Au, appears to be tetragonal in the ordered state. The transformation in Cu_3Pd is so sluggish that it may be possible to prove the existence of Bethe's local order by direct methods, quenching and annealing from a temperature above the critical temperature.

The relation between size of antiphase nuclei as measured by X rays and their influence on electrical resistance is being studied.

REFERENCES

(1) Bradley, A. J. and Jay, A. H. *Proc. roy. Soc.* A, **136**, 210 (1932).
(2) Bradley, A. J. and Jay, A. H. *J. Iron Steel Inst.* **1**, 339 (1932).
(3) Bradley, A. J. and Rodgers, J. W. *Proc. roy. Soc.* A, **144**, 340 (1934).
(4) Sykes, C. and Evans, H. *Proc. roy. Soc.* A, **145**, 529 (1934).
(5) Bragg, W. L. and Williams, E. J. *Proc. roy. Soc.* A, **145**, 699 (1934).
(6) Sykes, C. and Bampfylde, J. W. *J. Iron Steel Inst.* **2**, 389 (1934).
(7) Sykes, C. *Proc. roy. Soc.* A, **148**, 422 (1935).
(8) Sykes, C. and Evans, H. *J. Iron Steel Inst.* **1**, 225 (1935).
(9) Bragg, W. L. *J. Inst. Met.* **56**, 275 (1935).
(10) Bethe, H. A. *Proc. roy. Soc.* A, **150**, 552 (1935).
(11) Bragg, W. L. and Williams, E. J. *Proc. roy. Soc.* A, **151**, 540 (1935).
(12) Williams, E. J. *Proc. roy. Soc.* A, **152**, 231 (1935).
(13) Peierls, R. *Proc. roy. Soc.* A, **154**, 207 (1936).
(14) Sykes, C. and Evans, H. *J. Inst. Met.* **58**, 255 (1936).
(15) Sykes, C. and Jones, F. W. *Proc. roy. Soc.* A, **157**, 213 (1936).
(16) Sykes, C. and Jones, F. W. *J. Inst. Met.* **59**, 257 (1936).
(17) Sykes, C. and Wilkinson, H. *J. Inst. Met.* (in the Press).
(18) Sykes, C. and Jones, F. W. *Proc. roy. Soc.* (in the Press).
(19) Bernal, J. *Trans. Far. Soc.* **33**, 27 (1937).

AGE-HARDENING ALLOYS

By C. H. DESCH, National Physical Laboratory

THE object of this short note is merely to call the attention of physicists to certain effects observed in alloys, of great technical importance, the explanation of which will have to be sought in the properties of the lattice, and in the changes of energy with temperature in lattices composed of more than one kind of atoms. The literature of the subject is very extensive, and has been reviewed by a number of recent writers.

The effect known as age-hardening, in which an alloy, after being heated and quenched, increases in hardness either spontaneously or on heating to a temperature below that of quenching, depends on the properties of supersaturated solid solutions. In order that an alloy may show this effect, it is essential that a solid solution be formed at a high temperature, from which a second phase can separate on cooling slowly. Quenching retains the solid solution in a supersaturated condition, and reheating causes precipitation, usually in a finely divided form. A marked change in solubility with temperature is essential, but the actual amounts vary widely in different alloy systems. Thus in the iron-nitrogen system the saturated solid solution contains only 0·05 per cent N at 700° C., whilst in the iron-molybdenum alloys the limit is 35 per cent at 1440°. Usually the quantity of the precipitated phase is only a small fraction of the solvent metal, but in the alloy of atomic composition Fe_2NiAl, studied by Bradley, the two phases which separate are in equal quantity.

Prolonged heating at a temperature below that of quenching leads to softening, and when the heating has been continued until particles of the second phase have reached such a size as to be easily visible under the microscope, the maximum hardness has always been passed. The original explanation of age-hardening by Merica, Waltenberg and Scott(9) was based on these facts. It was supposed that precipitation began in the form of very minute particles, and that these agglomerated with continued heating, a certain critical dispersion, below the limits of visibility in the microscope but not otherwise defined, producing the greatest hardness. In broad outline, this view still holds good, at least for those alloys which are hardened by heating, although minor modifications have become necessary. The chief difficulties in its application have arisen in dealing with alloys which harden at atmospheric temperatures, including those light alloys of aluminium in which the effect was first discovered. The nature of the later stages, in which agglomeration and softening take place, is not disputed, but there are differences of opinion regarding the processes which occur before the appearance of detectable particles.

In most age-hardening systems, the phase which can separate on slow cooling is a compound of the two metals, or at least an intermediate phase composed of two kinds of atoms. There is, however, one important exception among alloys which have been studied in detail. This is the system copper-silver, in which hardening occurs by the separation of the pure metals. Copper and silver have identical space lattices, although their atomic diameters differ by 13 per cent, yet appreciable hardening can occur on suitable treatment. Any explanation of age-hardening must account for this simple case as well as for those in which precipitation of a new intermediate phase can occur. The hardening effect is considerable, an alloy with 6·6 per cent of copper, for instance, increasing from 50 to 140 Brinell at 250°(12).

The first objection to the simple hypothesis of hardening by critical dispersion came from determinations of the electrical resistance during the process. The quenched alloy, being a supersaturated solid solution, usually has a higher resistance than the same alloy in the annealed state, when separation into two phases is complete. Any partial separation, as required by the hypothesis of dispersion, might then be expected to cause a fall in resistance. This actually occurs with many alloys, but duralumin was found by Fraenkel(2, 3) to show an initial increase when aged at atmospheric temperature, decreasing normally later. This fact, confirmed for some other alloys, including those of aluminium with small quantities of copper, caused Konno, Fraenkel, Sachs and others to maintain that hardening was caused by the movement of dissolved atoms to new positions in the lattice, favourable to the production of molecules, but causing local strains, thus increasing both hardness and electrical resistance. Rosenhain(10) suggested that, taking the original view, the first production of ultra-microscopic particles would produce such local strains in the lattice as to account for the increase in resistance, thus to some extent reconciling the two views, as the critical dispersion might even be on a molecular scale.

The increase of resistance in the early stages of hardening is not confined to those alloys which "age" at atmospheric temperatures. It is well marked in the alloys of copper with beryllium(8), in austenite containing titanium(13) and in several systems, mentioned below, which are not usually classed as age-hardening, but in which an increase of hardness accompanies precipitation.

The maximum resistivity, when it occurs, is reached before the maximum hardness, and, as shown by Masing, Köster, and others, when various properties which change during ageing are plotted against the time, the maxima do not coincide. It has also been shown by Gayler(5) and by Cohen(14) that two maxima may sometimes be found in the hardness-time curve.

Gayler and Preston(4) regarded the process as taking place in two stages: (1) the rejection of atoms of the dissolved metal from the lattice of the solid solution, with the formation of chemical molecules in certain instances, and (2) the coagulation of these atoms or molecules to form discrete particles. A more elaborate view of the process has since been given by Gayler(5). Tammann(11) considered that the rejected atoms must collect on certain planes of the parent lattice, and that only when many neighbouring planes are so occupied can precipitation occur. This view has been confirmed by much later work by Mehl, Masing, Fink and others, which shows that the particles tend to group themselves to form minute plates or needles parallel with certain crystalline planes or directions in the parent lattice.

The main process is clearly one of diffusion. In accordance with this, when the logarithm of the time taken to reach a maximum value of a property, such as hardness, is plotted against the reciprocal of the absolute temperature, a straight line is frequently obtained(7). The initial stage of the process is, however, the reverse of diffusion (which always tends towards greater homogeneity) since it involves the segregation of certain atoms from a lattice on which they are distributed with statistical regularity. This process is not confined to age-hardening alloys, but must occur whenever one solid phase separates from another. The metallurgist, then, seeks an answer from the physicist to this question: what are the forces which lead to the expulsion of certain atoms from the lattice of a solid solution when the temperature falls to a certain point or when, the solid solution having been preserved in a supersaturated condition by quenching, the temperature is raised? (Alloys which harden at atmospheric temperature fall under this condition, as they are quenched at a lower temperature and do not harden if kept sufficiently cold, as, for instance, when quenched duralumin rivets are preserved in the soft state in solid carbon dioxide.)

The conditions are different from those of a solid crystallising from a liquid. The formation of nuclei of the solid phase by chance collisions is easily understood, but the movement of metallic atoms over a distance of many lattice spacings, making the structure less homogeneous, is more difficult to picture. It must occur very locally, since in the early stages no change in the lattice parameter can be detected by means of X rays.

In the discussion on Dr Gayler's paper(5), Prof. Mott remarked that groupings of, say, five atoms each would have a marked effect in increasing the electrical resistance of the lattice, so that the maximum resistance found in many, but by no means all, age-hardening alloys, must correspond with a very early stage in the formation of nuclei. Such nuclei once formed and the statistical uniformity of the lattice having been destroyed, local concentration gradients exist, and the rest of the process may be looked on as one of diffusion, the growth of the ultramicroscopic particles and their union to form larger masses being one which is very familiar in metallographic studies. The next question is, at what stage in the process will the greatest elastic strains be set up in the lattice, tending to increase the hardness and, to a lesser degree, the electrical resistance?

When the phase which is ultimately precipitated is composed of two kinds of atoms, as in hardening caused by $CuAl_2$, Mg_2Si, or Cu_3Be, what the chemist has been accustomed to call chemical affinity may be supposed to encourage the formation of groups approaching simple atomic ratios, but the separation of nuclei of copper from silver, or of silver from copper, cannot be accounted for in this way, yet the mechanism seems to be the same in each case. (That in the silver-copper alloys no increase in electrical resistance occurs during ageing, is probably due to the close similarity of the silver and copper atoms.) Both in the simple and in the complex examples, the separation occurs along the most closely packed planes in the lattice, and, in those alloys which have been examined in detail, in such a way that the new phase, when formed, is produced with a minimum rearrangement on those planes, so producing *Widmanstätten* structures on a small scale.

There is reason to believe that nuclei of appreciable size exist long before a change in the parameter can be detected by X rays. It must be emphasised that the segregations are very local, leaving the greater part of the lattice unchanged. Such changes in the quantity of background scattering as have been recorded are consistent with such a picture of the process. It is remarkable that chemical methods seem to be capable of detecting an earlier stage. It was first noticed that in the hardening of the beryllium-copper alloys the etching properties were altered at a very early stage, so that, although no separate particles could be seen under the microscope, lines parallel with (111) planes darkened on etching, producing a fine network, indicating a precipitation of ultra-microscopic particles. The same thing is seen in silver-copper alloys, and it is probably responsible for the characteristic etching properties of martensite in steels. That it could not be seen in the light alloys of aluminium was used as an argument for the special character of the hardening process in them, but the writer has always attributed its absence to the lack of delicacy of the methods in use for etching aluminium. Fink and Smith(1) found that in a light alloy containing 5 per cent of copper, precipitation could be seen after heating for an hour at 100°, whilst 34 hours at that temperature were required to produce a measurable change in the lattice parameter. Even at atmospheric temperature precipitation could be seen after three months, which is of course much longer than is needed to produce hardening, but indicates that the process is of the same kind as at higher temperatures. Aluminium containing magnesium gave similar results.

This hurried survey of the age-hardening problem leaves out many complications—the effects of heating to a higher temperature after partly ageing at a lower, and so on—but it is suggested that the mechanism of age-hardening may not be very complex. The original theory was probably too simple, in that it considered only changes in the sizes of the dispersed particles, and did not take account of how those particles came into existence, but in the writer's view it remains essentially true, although the critical dispersion must now imply a stage earlier than that at which it is proper to speak of a distinct phase. The work on order-disorder changes has made us familiar with systems in which local rearrangements can occur without producing a second phase in the ordinary sense.

The complex changes in age-hardening may then be due only to the progressive growth of nuclei formed by the rejection of certain atoms from the lattice. The electrical resistance seems to be most affected by the formation of groups of only a few atoms, the hardness by groupings of a rather larger size, and so on. (The subsequent fall of resistance and later of hardness as the groups grow larger presents no difficulty.) Effects on the magnetic properties are not produced until still later(15, 16). It is the initiation of the process, as mentioned above, that is difficult to picture, on which the advice of physicists is sought. The next problem is that of applying to age-hardening systems the same quantitative treatment that has proved successful in dealing with order-disorder transformations (Bragg and Williams, Borelius, Peierls, Sykes, etc.), so that it may be possible to predict the behaviour of a given system under given conditions of supersaturation.

A new phase separating from a solid solution does not always assume a dispersed form. The α phase in brass, for instance, separates on cooling the supersaturated β solid solution in large crystals. Nevertheless, it must pass through the preliminary stage of forming minute nuclei, and in its behaviour it then closely resembles an age-hardening system(6) although its supersaturated solid solution has a lower, and not a higher, electrical resistance than the two-phase system which is ultimately formed. It would seem that in these alloys the growth of nuclei to form distinct crystals is very rapid. Differences in what may be called the crystal habit of the precipitated particles account for many differences between alloys, and the reasons for such differences must be sought in the mechanism of the separation of the original particles and their subsequent growth.

REFERENCES

(1) Fink, W. L. and Smith, D. W. *Metals Technology*, **3**, (4) (1936); *Tech. Publ. Amer. Inst. Min. Engrs*, No. 706.
(2) Fraenkel, W. and Scheuer, E. *Z. Metallk.* **12**, 427 (1920).
(3) Fraenkel, W. and Seng, R. *Z. Metallk*, **12**, 225 (1920).
(4) Gayler, M. L. V. and Preston, G. D. *J. Inst. Met.* **41**, 191 (1929).
(5) Gayler, M. L. V. *J. Inst. Met.* **60**, 55 (1937).
(6) Hansen, M. *Z. Phys.* **59**, 466 (1930).
(7) Jenkins, C. H. M. and Bucknall, E. H. *J. Inst. Met.* **57**, 141 (1935).
(8) Masing, G. *Arch. Eisenhüttenw.* **2**, 185 (1928–9).
(9) Merica, P. D., Waltenburg, R. G. and Scott, H. *Sci. Pap. U.S. Bur. Stand.* No. 347 (1919).
(10) Rosenhain, W. *Chem. metall. Engng*, **28**, 899 (1923).
(11) Tammann, G. *Z. Metallk.* **22**, 365 (1930).
(12) Ageew, Hansen and Sachs. *Z. Phys.* **66**, 350 (1930).
(13) Hensel, *Trans. Amer. Inst. Min. Engrs.* **95**, 255 (1931).
(14) Cohen, M. *Metals Technology*, 1936, **3** (7); *Tech. Publ. Amer. Inst. Min. Engrs*, No. 751.
(15) Köster, *Arch. Eisenhüttenw.* **2**, 503 (1928–9).
(16) Eilender, Fry de Gottwald. *Stahl u. Eisen*, **54**, 554 (1934).

DISCUSSION OF THE PAPERS BY BORELIUS, BRAGG, DESCH

Reported by N. F. MOTT

In the discussion Prof. Bragg emphasized the contrast between the order-disorder change, which extends over a finite range of temperatures, and the change from liquid to solid, which is sharp. He drew the attention of the conference to some speculations by Bernal* which attempt to show that intermediate states between liquid disorder and crystalline order would have very high energy and therefore do not occur.

Prof. Simon did not agree with Bernal's conclusion that no intermediate phase between solid and liquid can exist.

Both Prof. Fowler and Prof. Bragg were critical of Prof. Borelius' use of the free energy diagram in his discussion of hysteresis in the segregation process (Borelius, § 10). A rough calculation by Prof. Bragg of the life-time of the metastable states envisaged by Borelius suggested that it should be considerably less than 1 sec.

An extension of Bethe's theory of the order-disorder transition by Fowler and Chang to include interaction between next nearest neighbours was announced (to be published). Dr Sykes reported some new measurements of the heat content of CuZn up to the critical temperature, which agreed better with the new calculations than with the old; the new theory contains however an arbitrary parameter. A theory by Mott† of the nature of the ordering force also gives some indication of the shape of the specific heat-temperature curve.

Dr Sykes also reported measurements of the heat content of MgCd, which shows a latent heat at the critical temperature, in disagreement with the theoretical expectations, and also for Cu_3Pd, which does *not* show the latent heat to be expected for an alloy where the two constituents are present in unequal amounts. This may be connected with the change of structure which takes place for this alloy at the critical temperature.

In connexion with Prof. Borelius' measurements of the resistance of nickel, Dr Potter mentioned some recent measurements of his own (to be published shortly in *Proc. phys. Soc.*)

Dr Bradley gave an account of his investigations on the ternary alloys of the system FeNiAl. For certain compositions, alloys of this system would, if cooled slowly, crystallize out as a two-phase system, *both* phases having the same body-centred cubic lattice structure but with very slightly different lattice spacing, so small that it is very difficult to detect by X-ray methods. One of the two phases is magnetic, the other is non-magnetic and shows a superstructure.

---

* *Trans. Faraday Soc.* **33**, 27 (1937).

† *Proc. phys. Soc.* **49**, 258 (1937).

If the alloy is cooled quickly (quenched) a single phase only is obtained. But if the alloy is cooled at a moderate rate, regions of undetermined size (say a hundred to a thousand atoms in length) form in the crystal, having the composition of one or other of the two phases that will eventually crystallize out, but arranged in a *single* body-centred lattice; they have not yet broken away and formed separate crystals with their individual lattice parameters. These regions must thus be highly strained; for their lattice parameters must necessarily be those of the parent lattice (i.e. the quenched alloy), whereas they would be in equilibrium only with different values of the parameters. Dr Bradley ascribed the properties which these alloys have as permanent magnets to this state of strain.

Prof. Bragg stated that the dispersion responsible for age hardening mentioned by Dr Desch must be understood in this way: groups of atoms having the compositions of the phases that eventually crystallize out would form, while still keeping to the old lattice. This would set up strains, and so produce hardening. The second process would be when these groups broke away from the parent lattice; this would decrease the internal strain, and thus the hardness.

Dr Peierls asked why the phase which is precipitated forms crystals with a plate-shaped structure parallel to a definite set of crystallographic planes. Two explanations seemed possible. The crystals might tend to form at internal surfaces of misfit, or cracks; this was favoured by Dr Desch. Prof. Bragg, on the other hand, considered that a given volume of a new phase could crystallize out with less strain to the surrounding medium if it took a plate-like structure than if it were, for example, round. He cited the case of felspar, which, if cooled, breaks up into bands containing alternately an excess of Na and of K. In this way the least strain is produced.

PART III

CONDUCTION IN THIN METALLIC FILMS

THE STRUCTURE OF THIN METALLIC FILMS

By G. I. FINCH

THE object of this paper is to draw attention to those structural features which are likely to give rise, at least in part, to the abnormally low conductance associated with thin metallic films(1). The more usual methods for preparing such films in reasonably uniform thickness are (i) cathodic sputtering, (ii) condensation from the vapour *in vacuo*, (iii) chemical deposition and (iv) evaporation of a colloidal solution. Beaten leaf is generally too thick and irregular to be of use in conductivity measurements, and although electrodeposits can usually be freed from the basis metal their further transfer without injury to a non-conducting substrate is difficult.

Electron diffraction has become the most searching method for the study of the structure of thin metallic films. In addition to revealing crystal structure and orientation, electron diffraction will generally afford some indication of other features which are often of too fine a detail to be seen under the microscope, such as crystal size and shape and the nature of the film surface texture.

Consider, for example, the pattern (figure 1) obtained with the electron beam at grazing incidence from a bismuth film electrodeposited on to a polished copper surface. We see that (i) the film is polycrystalline; (ii) the crystals are unorientated; (iii) the pattern dimensions agree with the known structure of bismuth; (iv) the absence of ring-broadening due to refraction towards the central spot shows that the diffraction rings are formed by transmission; thus the diffracting portions of the crystals must project above the surface; (v) the ring definition suggests a size of effectively diffracting crystal projections exceeding 100 A. in directions normal to the beam but, in view of the clearness of the pattern and absence of general background, not exceeding about 200 A. in the beam direction; (vi) the granulated appearance of the rings shows that a relatively small number of crystal projections are diffracting, which suggests that the crystals are large enough to be seen in the microscope. Thus we can picture the general structure of the bismuth film as consisting of disordered array of fairly large crystals terminating in spikes projecting above the mean level of the surface, an impression which would be confirmed if a sharp and strongly granulated ring pattern were obtained by transmission through the film after its being detached from the substrate. It will readily be seen that if the average thickness of the film were only 10 A., the actual crystals could not cover more than one-tenth of the surface, and the film would be discontinuous apart from small areas of contact between neighbouring crystals. Electron diffraction shows that the structure of very thin metallic films with an average thickness of the order of 50 A. and less is in general of this type.

Again, from figure 2, yielded by a platinum fibre sputtered in argon on to a polished glass disk, we see that the platinum crystals are strongly orientated with a cube face parallel to the substrate. The increase in width of the arcs which occurs as the pattern centre is approached is evidence of a refractive effect and shows that the pattern has been formed partly by reflection, i.e. entry and exit of the beam through the same flat crystal faces, in this case (001) faces; since the individual diffractions are not wholly displaced but are spread out between the normal and refracted positions, it is clear that diffraction through projecting crystalline spikes of a wide range of acuteness also occurs. The same film by transmission with the beam normal to the surface gives a complete ring pattern in which the *hko* diffractions are abnormally strong. The rings show no signs of granulation and their width is such as to suggest a mean crystal size of the order of 50 A.

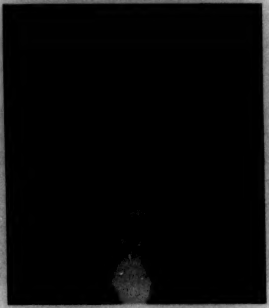


Figure 1.

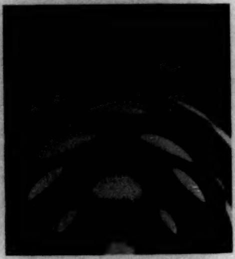


Figure 2.

Caution is necessary in the estimation of crystal size from ring-breadth, especially in the case of reflection patterns. Thus, suppose a metal film of uniform thickness be deposited on a plane surface, the diffraction rings will be very broad, even though the crystals may be large, provided the deposit crystals form such obtuse-angled projections that only a small extent of each projection is thin enough to contribute to the diffraction of the beam. In such a case, if the film is sufficiently thin, a transmission pattern will give a better idea of the crystal size, and will confirm whether the diffuseness of the rings of the reflection pattern is due to the obtuseness of the crystal projections or to small crystals. On the other hand, a reflection pattern is likely to give a better impression of the particle size if the substrate surface be spiky and is more or less uniformly covered by the deposit.

Several workers(2) have ascribed the anomalous conductivity of thin films, prepared as a rule by cathodic sputtering or evaporation, to their supposed amorphous nature. Electron diffraction results negative this view; thus it has been found generally that cathodically sputtered and evaporated metallic films are invariably crystalline, even when deposited at liquid-air temperatures(3). There is, however, a pronounced tendency for the crystal size to increase with the temperature of the substrate during deposition. Sputtered films often contain occluded gas, or the metal may even combine with gas in the process of deposition, though by sputtering in carefully purified argon this effect can be reduced⁽⁴⁾. The presence of gas in sputtered films no doubt explains the disappearance of the reflection diffraction pattern from sputtered platinum films during heating *in vacuo*, a result which was first attributed by Finch and Ikin to a reduction in crystal size. More recent experiments in which such heated platinum films were floated off the glass or quartz substrate by a weak solution of hydrofluoric acid revealed, however, a well-developed crystal structure, in that the films yielded sharp ring patterns on transmission. Hence it seems clear that the fading of the initial reflection pattern with heating must have been due to a collapse of the projecting diffracting crystal spikes as a result of the evolution of gas occluded during sputtering, a view which is confirmed by the fact that we have found that platinum films formed by evaporation *in vacuo* give reflection patterns which are virtually unaffected by heating. In view of the uncertainties introduced by the presence of occluded, and often also by combined, gas, sputtered films can hardly be regarded as suitable for critical conductivity determinations.

The structure of films condensed *in vacuo* may be profoundly affected by the nature of the substrate. A pseudomorphic lattice change has only been observed in the case of metals of similar lattice constants and crystal structure in contact as substrate and deposit, and this complication from the point of view of conductivity measurements is therefore easily avoided. Crystalline substrates consisting of natural or cleavage faces of ionic single crystals are rarely, if ever, sufficiently smooth, and in addition they often exert very strong orientating effects. For example, most metals deposited on a suitably heated rock-salt cleavage surface are strongly orientated and may even form single crystal sheets with an orientation governed by the substrate⁽⁵⁾. In view of the difference between the metal and rock-salt lattice dimensions it is most unlikely that such sheets are true single crystals; more probably they consist of a mosaic of small crystals of like orientation. Further, in the case of rock-salt and similar cleavage surfaces, it is a moot point as to how far the substrate mosaic structure, cleavage striations and cracks may affect the continuity of the deposit film. On the other hand, extremely smooth non-conducting substrate surfaces, free in all probability from surface flaws and cracks, can be obtained by polishing; for example, the diffraction patterns obtained from polished diamond, quartz, sapphire and many other surfaces are such as to suggest that they are exceedingly smooth and crystalline, whilst polished fused quartz, glass, spinel and other surfaces give patterns which are characteristic of a liquid or vitreous surface⁽⁶⁾.

While the orientation which occurs in a deposit formed on a single crystal surface may easily be complete in the sense that both directions of orientation of the deposit are controlled by the structure of the substrate, a twofold orientation has apparently never been observed on a vitreous surface, although an alignment of the deposit crystals with one plane parallel to the substrate surface is so often noticed as to be the rule rather than the exception, particularly if the substrate was suitably heated during deposition.

It frequently happens that the useful life of a thin metallic film ends with the appearance of a fine network of cracks which in some cases may be due to a differential expansion as between deposit and substrate, and in others to contamination of the deposit by traces of organic materials(7). Recent electron diffraction work has shown how easily contamination can occur with greases and mercury vapour(8); hence in the preparation of thin metallic films for conductivity purposes the greatest possible care should be taken to eliminate such impurities. Lovell's(1) recent experiments have shown the great gain in reproducibility of results which follows when proper precautions are taken to eliminate such impurities and gas adsorption. Some workers have observed deviations from the normal lattice constants in thin films. Thus Riedmiller and Cosslett(9) found such an effect with indium and attributed it to gas occlusion: and Quarrell(10) has found similar deviations of lattice dimensions to be general in the initial layers of a deposit and, in the case of face-centred-cubic metals, attributed this to a gradual transition from a hexagonal close-packing of the atoms first deposited to the normal face-centred-cubic packing.

Ample evidence has been obtained for the rapid oxidation of evaporated metal films on exposure to air. Thus Finch and Quarrell(11) found such oxidation with zinc and magnesium, Beeching(12) with aluminium and copper, Riedmiller(9) with nickel, and Nelson(13) with iron. Thin metal films, especially when prepared by evaporation, are much more prone to oxidation than the surface of the metal in bulk. Beeching considers that oxygen may be taken up from the surface of the substrate, where it is present as an absorbed layer; this points to the importance of careful cleaning and degreasing of the substrates employed.

To sum up: For conductivity experiments it would seem advisable to use suitable highly-polished non-conducting substrates. Deposition should be carried out in a high vacuum, the necessary precautions being taken to prevent contamination by either grease, mercury or gas. Wide temperature fluctuations of the substrate should also be avoided both during preparation and use. It should not be difficult to determine the resistance of a film *in vacuo* and thus eliminate errors and uncertainties arising from gas adsorption or compound formation.

REFERENCES

(1) Féry, A. *J. Phys. Radium*, **4**, 301 (1933); *Ann. Phys.*, Paris, **19**, 421 (1933).
Jagersberger, A. *Z. Phys.* **87**, 513 (1934).
Deubner, A. *Ann. Phys.*, Lpz., **20**, 449 (1934).
Bosworth, R. C. L. *Trans. Faraday Soc.* **30**, 549 (1934).
Townes, E. and Roller, D. *Phys. Rev.* **47**, 197 (1935).
Murman, H. *Z. Phys.* **89**, 426 (1934).
Kramer, J. *Ann. Phys.*, Lpz., **19**, 37 (1934).
Johnson, M. C. and Starkey, T. V. *Proc. roy. Soc.* A, **140**, 126 (1933).
Lovell, A. C. B. *Proc. roy. Soc.* A, **157**, 311 (1936); *Proc. phys. Soc.* **49**, 89 (1937).
Appleyard, E. T. S. and Lovell, A. C. B. *Proc. roy. Soc.* A, **158**, 718 (1937).
Suhrmann, R. and Berndt, W. *Phys. Z.* **37**, 146 (1936).

McLennan, J. C., Burton, A. C., Pitt, A. and Wilhelm, J. O. *Proc. roy. Soc.* A, **138**, 245 (1932).
Misener, A. D. and Wilhelm, J. O. *Trans. Roy. Soc. Canada*, **29**, 5 (1935).
Misener, A. D., Wilhelm, J. O. and Smith, H. G. *Trans. Roy. Soc. Canada*, **29**, 13 (1935).
Cosslett, V. E. *Proc. phys. Soc.* **49**, 121 (1937).
(2) Zahn, H. and Kramer, J. *Z. Phys.* **86**, 413 (1933).
Suhrmann, R. and Berndt, W. *Phys. Z.* **37**, 146 (1936).
(3) Hass, G. *Naturwissenschaften*, **25**, 232 (1937).
(4) Finch, G. I., Murison, C. A., Stuart, N. and Thomson, G. P. *Proc. roy. Soc.* A, **141**, 414 (1933).
Finch, G. I. and Ikin, A. W. *Proc. roy. Soc.* A, **145**, 551 (1934).
(5) Lassen, H. *Phys. Z.* **35**, 172 (1934).
Kirchner, F. and Lassen, H. *Ann. Phys.*, Lpz., **24**, 113 (1935).
Bruck, L. *Ann. Phys.*, Lpz., **26**, 233 (1936).
Cochrane, W. *Proc. phys. Soc.* **48**, 723 (1936).
(6) Finch, G. I. *Nature*, Lond., **138**, 1010 (1936).
(7) Tanaka, S. *Rep. Aero. Res. Inst. Tokyo*, **11**, 369 (1936).
(8) Mark, H., Motz, H. and Trillat, J. J. *Naturwissenschaften*, **20**, 319 (1935).
Aylmer, A. E., Finch, G. I. and Fordham, S. *Trans. Faraday Soc.* **32**, 864 (1936).
(9) Riedmiller. *Z. Phys.* **102**, 408 (1936).
Cosslett, V. E. *Proc. phys. Soc.* **49**, 121 (1937).
(10) Quarrell, A. G. *Proc. phys. Soc.* **49**, 279 (1937).
(11) Finch, G. I. and Quarrell, A. G. *Proc. roy. Soc.* A, **141**, 398 (1933).
(12) Beeching, R. *Phil. Mag.* **22**, 938 (1936).
(13) Nelson, H. R. *J. chem. Phys.* **5**, 252 (1937).

SOME FACTORS INFLUENCING THE RESISTANCE OF THIN METAL FILMS

By E. T. S. APPLEYARD

§ 1. INTRODUCTION

A CONVENIENT summary of the early work on thin metallic films, performed prior to 1928, is provided by Bartlett[(1)]. The observations varied profoundly not only from one worker to another but also in the experiments of the same investigator performed under similar experimental conditions. As a result of these discrepancies, which arose partly from primitive technique and partly from uncontrolled factors whose importance was not then understood (condition and temperature of the substrate, adsorbed gas, etc.), various *ad hoc* hypotheses were produced to explain particular experiments and little advance was made towards obtaining experimental conditions which would give consistent and reproducible results. It would be useless to add to the already copious literature of speculation upon these early observations. This review is, therefore, confined to enunciating briefly and attempting to explain some of the chief experimental observations on the resistance of thin metal films prepared by evaporative deposition in a good vacuum. This method of preparation curtails considerably the number of arbitrary factors which can influence the resistance of the films; and in particular it gives some hope of minimising, if not eliminating, the effects due to adsorbed gas.*

§ 2. TYPICAL EXPERIMENTAL RESULTS

A usual and important type of experiment consists in allowing a calibrated beam of metal atoms to fall upon a cooled surface. Suitable electrical contacts allow the resistance of the film to be measured at frequent intervals as the deposition proceeds, and in this way the relationship between the nominal resistivity† and the nominal thickness† of the film can be obtained experimentally.

Typical of the results obtained by evaporation are those of Reinders and Hamburger[(2)]. These workers paid attention to the temperature of the depositing surface and they worked in a tolerable vacuum probably of the order of 10^{-6} mm. of mercury. (Nevertheless the apparatus could not be properly baked out since it contained greased joints.) The thickness of the deposits was obtained by chemical estimation of the evaporated silver, thus avoiding recourse to speculative formulae which have been used in certain cases.

---

* Nevertheless, even in the best available vacuum, say 3×10^{-8} mm. of mercury, 10^{13} atoms per second strike every square cm. of the internal surface of the apparatus if the residual gas is oxygen. This rate is quite comparable with the rate of condensation of metal atoms in most experiments.

† The nominal thickness of a film is the thickness calculated from the expression $t = m/\rho$ where m = mass of metal per unit area. It only coincides with the geometrical thickness when the film is uniform and has the same density as the bulk metal. The nominal resistivity is calculated by assuming that the nominal thickness is in fact the true thickness. Where we refer to "thickness" and "resistivity" without qualification they are assumed to be derived in this way.

Figure 1, copied from the paper of Reinders and Hamburger, shows the results obtained for silver. Ordinates are logarithms of nominal resistivity in ohm-cm., abcissae are logarithms of the thickness in multiples of 10^{-7} cm. Curve a_3b_3 is the resistivity of silver deposited at room temperatures (300° K.), a_1b_1 deposition at 88° K., a_2b_2 the {resistivity, thickness} relation of films deposited at 88° K. and afterwards raised to room temperatures. For comparison the results of earlier workers are also sketched in; Vincent$^{(3)}$ (chemical deposition, 1901); Pogany$^{(4)}$ (sputtered films, 1916); Weber and Oesterhuis$^{(5)}$ (evaporation, 1916).

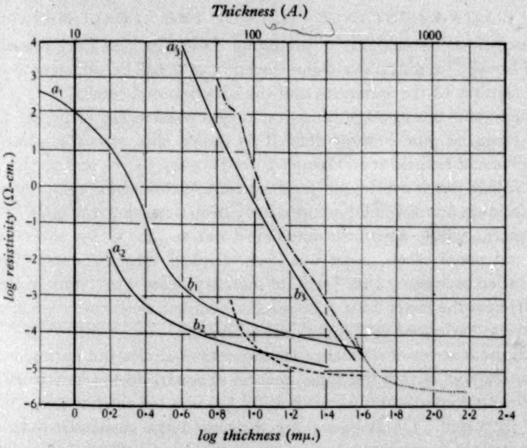


Figure 1. •—•—•—Weber-Oesterhuis; ———— Pogany; •••••• Vincent.

It will be seen that Reinders and Hamburger were successful in obtaining detectable conductivity at only 6 A. thickness, or about two atomic layers. Nevertheless two important features stand out characteristic of all previous work on thin films.

The first is that the resistivity of films less than 100 A. in thickness is from 10^7 to 10^8 times that of the metal in bulk. The second is that the resistivity of the films alters irreversibly on heat treatment by a factor of about ten. Also deposition at 300 K. gives conductivity only at nominal thicknesses greater than 40 A. Reinders and Hamburger suppose that granulation of the film at the higher temperature accounts for this delayed conductivity, but they assume other causes to account for the high resistance of films deposited at 88° K. Before discussing the evidence for their interpretation we propose to describe in brief the results of certain experiments recently carried out in this laboratory on thin films of the alkali metals. These results we believe to be interesting from two points of view: Firstly, because we believe that they are the only metal films ever prepared which can be obtained completely coherent in layers less than 50 A. thick; secondly, because by suitably varying the experimental conditions we have been able to prepare films of any resistivity desired from the extremely low value shown by the coherent films to values 10^5 times greater. We advance reasons for believing that these high resistivities are due to granulation or agglomeration of the film, and that agglomeration may account for both the delayed conductivity and the high resistivity of films prepared by many other workers, though further experiments are needed to decide definitely upon this point.

§ 3. LOW-RESISTANCE FILMS OF THE ALKALI METALS

The experimental methods of preparing these films are fully described in the papers of Lovell(6) and Appleyard and Lovell(7), so it will be sufficient to summarize the chief features of the apparatus and the experimental results.

The apparatus consisted of a molecular gun constructed of pyrex. The stream of atoms from the gun, suitably defined by cooled slits, struck a surface of pyrex glass which could be held at any temperature between 64° K. and 90° K. Here they formed a square patch overlapping end contacts of colloidal graphite spread upon a layer of platinum paint which had previously been burnt into the glass. Prior to any experiment the whole apparatus was baked out at 500° C. for several hours and carefully outgassed alkali metal was then distilled into the oven. The residual pressure varied between 5×10^{-7} mm. of mercury and 5×10^{-8} mm. of mercury and was usually near the lower limit. The results described below were not apparently at all sensitive to variations of this residual pressure.

A continuous series of resistance measurements carried out during and after the deposition showed always the same general character in the case of all the alkali metals. The resistance and the resistivity of the film fell steadily as the thickness of the layer increased. On stopping the deposition the resistance did not remain constant as was to be expected, but rose smoothly so as to increase by a factor of ten or more when the condensing surface was kept at 90° K.

But in the early experiments with rubidium, a consistent value could be obtained at first neither for the value of the resistance nor for the subsequent increase of resistance after deposition was stopped, and a series of experiments carried out under apparently the same conditions gave extravagantly different results, varying by factors of many hundred. The residual pressure and small variations of beam intensity proved to have no critical effect, and it was not until a casual observation forced upon our attention the important role of the surface conditions of the substrate that we were able to obtain consistent results. In Lovell's paper the technique of prolonged local baking necessary to produce a standard surface, upon which results consistent to 3 per cent could be obtained, is fully described.

The general character of the anomalies observed is best illustrated by showing the effect of deliberate contamination upon a surface previously baked to the standard state. Figure 2*a* reproduced from the *Proceedings of the Royal Society*(6) shows the effect of CO_2 contamination upon a standard surface. The pressure in the apparatus was raised to 10^{-6} mm. of CO_2. The pressure was held at this value for some minutes, evolution of CO_2 was stopped, and as soon as the vacuum had reached its original value a distillation was commenced. Throughout the process the surface and defining slits were held at 90° K. The first distillation after this treatment gave no conductivity after 30 min. distillation of rubidium at the rate of $3 \cdot 18 \times 10^{12}$ atoms per cm.^{2} per sec.

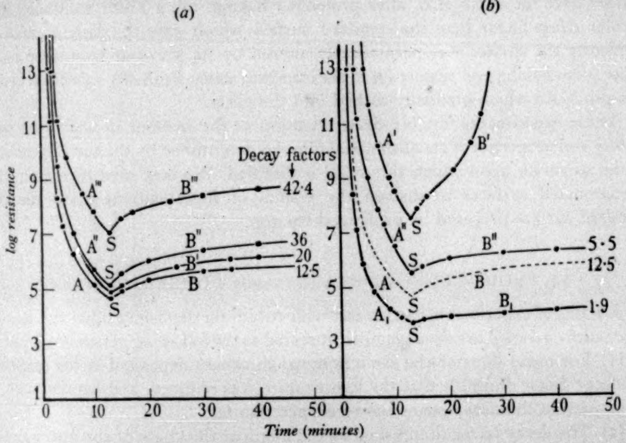


Figure 2.* Influence of contaminated substrate on the formation and decay of conductivity for films 21·8 A. thick deposited at 90° K. with beam intensity $3 \cdot 18 \times 10^{12}$ atoms/cm.^{2}-sec. (*a*) Influence of varying amounts of CO_2 impurity. (*b*) Influence of varying amounts of H_2O impurity. S, shutter closed (cessation of deposition); - - - - standard surface curve for comparison.

[*By the courtesy of the Royal Society*

Table I below shows the results obtained by successive baking of the substrate.

Table I

Experimental curve	Total baking time before distillation (hours)	Remarks
A''' *B'''*	1	
A'' *B''*	20	
A' *B'*	40	
AB	80	Identical with results obtained on standard surface

The numbers to the right of the curves are the so-called decay factors, an arbitrary measure of the instability of the films. The factor is defined as $\Delta R/R$ where ΔR is the change in resistance during the half hour after stopping distillation, and R

---

* The decay factors are inserted at the right-hand side of all decay curves.

is the resistance when the deposition is stopped. The most important feature of the curves is their steady alteration as the heat treatment is continued, and the fact that they converge finally to the value characteristic of the standard surface after prolonged heat treatment of the surface.

Figure 2*b* represents the results of a series of experiments when water vapour and not CO_2 was the contaminating agent. $A'B'$, $A''B''$ represent successive curves obtained at different stages of the baking. The final steady state of the surface gave the curve A_1B_1 after prolonged baking, i.e. a lower resistance and a smaller decay factor than the standard surface which gave the dashed curve AB. Evidently the surface was permanently altered by its previous treatment and no subsequent baking ever restored it to the standard state. Probably rubidium hydrate was produced which gradually soaked into the glass.

These experiments forcibly draw attention to the manner in which the whole history and properties of an alkali metal film are determined by the surface condition of the substrate upon which the metal is distilled. We may now turn from these contaminated surfaces to discuss the results of investigations upon the clean standard surface prepared by prolonged baking.

§ 4. PRODUCTION OF STABLE AND COHERENT FILMS

A series of experiments carried out with rubidium deposited upon the standard pyrex surface cooled to various temperatures led to the following general conclusions:

(1) For metal films of the same nominal thickness deposited at the same rate, the decay factor diminished as the temperature was reduced, and parallel with this diminution of the decay factor the resistance also fell.

(2) The decay factor diminished as the nominal thickness of the film increased for deposition at a given temperature.

(3) By deposition at 64° K. (the lowest temperature available in the experiments) it was found possible to prepare completely stable films provided the nominal thickness exceeded 40 A. These films remained stable when afterwards raised to 90° K. though a film of this nominal thickness deposited at the higher temperature had the large decay factor of 3·5.

Figure 3 summarizes the results for rubidium.

Potassium and caesium give results of the same general character, except that potassium films were less stable and caesium films more stable than those of rubidium. The case of caesium is particularly interesting, for in this case by deposition at 64° K. stable films of nominal thickness only 5·7 A. were obtained. It was, however, not possible to determine the temperature coefficients of films as thin as this since they began to decay slowly when raised to 90° K. Another curious anomaly exhibited by the caesium films, in which they differ completely from those of potassium and rubidium, is that when deposited at any definite temperature the stability appears to be greater for films of 5·7 A. than it is for those of 24 A. After this thickness the films become more stable again as the thickness increases.

§ 5. RESISTIVITIES OF THE STABLE FILMS

The most obvious peculiarity of these films as compared with those prepared by all previous workers is their low resistivity at thicknesses below 100 A. For example, reference to figure 1 of this account shows that the silver films prepared by Reinders and Hamburger$^{(2)}$ had resistivities more than 1000 times those of the bulk metal at a thickness of 40 A. Caesium films of this thickness deposited at 64° K. had only 5 times the resistivity of the bulk metal. Figure 4 below is a graph showing experimental resistivities plotted against nominal thickness for caesium deposited at 64° K. (full curve). Conductivity was first detectable at a nominal thickness of only 0·35 A. or 0·06 atomic layers. These facts lead us to believe that perhaps the films could be regarded to a first approximation as coherent slices of a crystalline, or polycrystalline, metal and that their resistivities (which were still higher than those

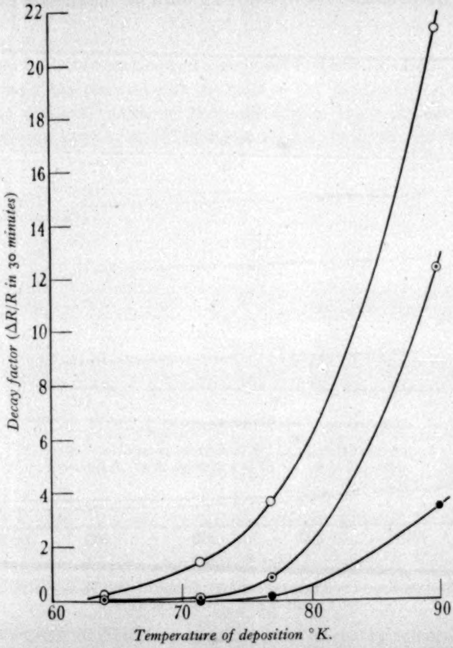


Figure 3. Decay factors as a function of the temperature of deposition for films of a given thickness deposited with beam intensity $3{\cdot}18 \times 10^{12}$ atoms/cm^2/sec. ○ 4·4 A.; ⊙ 21·8 A.; ● 43·6 A.

[*By the courtesy of the Royal Society*

of the bulk metal) could be accounted for by assuming that the mean free path of the conduction electrons was effectively shortened by collision with the boundaries; an idea originally due to J. J. Thomson⁽⁸⁾, who gave a formula for the resistivity to be expected.

Hamburger⁽⁹⁾ had already applied Thomson's formula to much thicker films than this. His calculations contain so many qualifications that they cannot be said to show more than a sudden rise of resistivity when the thickness of the film became comparable with the mean free path calculated on his assumptions. In any case, Thomson's formula was not applicable to our films, for in all cases the thickness here is very much less than the mean free path in the bulk metal, and Thomson took no account of the fact that, under these circumstances, most of the collisions will take place at the boundaries.

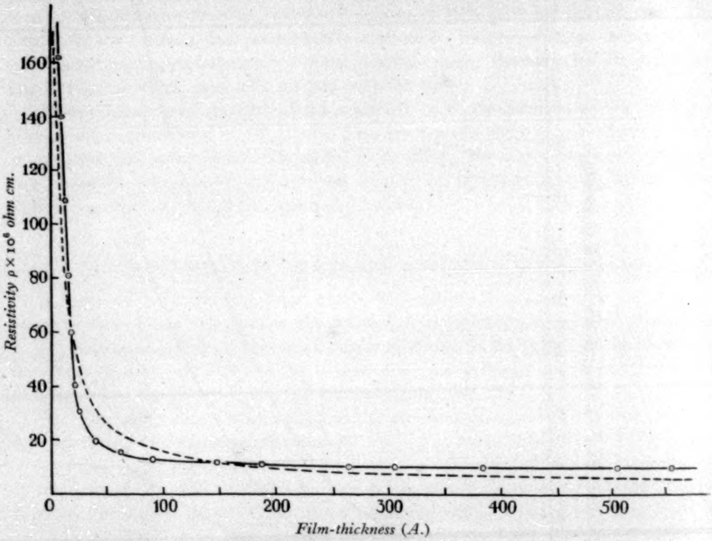


Figure 4. Theoretical - - -, and experimental ⊙. Resistivity/thickness curves up to 550 A. for a caesium film deposited at 64° K.

[By the courtesy of the Royal Society

A modified formula⁽⁶⁾ with which we have compared our results is

$$\frac{\sigma_t}{\sigma_\theta}=\frac{t}{\lambda_\theta}\left(1+\log\frac{\lambda_\theta}{t}\right) \qquad \ldots\ldots(1),$$

where σ_t is the resistivity of the film and σ_θ that of the bulk metal at the same temperature θ. λ_θ is the mean free path in the bulk metal, and may be deduced from the observed resistivity by the formula$^{(10, 11, 12)}$

$$\frac{1}{\sigma}=\frac{Ne^2}{m}\frac{2\lambda_\theta}{v},$$

where N is the number of electrons (atoms) per unit volume and v the velocity of the electrons, given by

$$v=\frac{h}{2m}\left(\frac{3N}{\pi}\right)^{\frac{1}{3}}.$$

The formula is derived making two assumptions: firstly that $t \ll \lambda_\theta$, and secondly that all collisions of the electron with the sides of the film are inelastic. The values of λ_θ are, using accepted values for the resistivity of the bulk metal, 1980 A. at 90° K. in rubidium, 1450 A. at 64° in caesium. All the films described here are less than 500 A. thick, though work with caesium films up to 12,000 A. is in progress (Lovell).

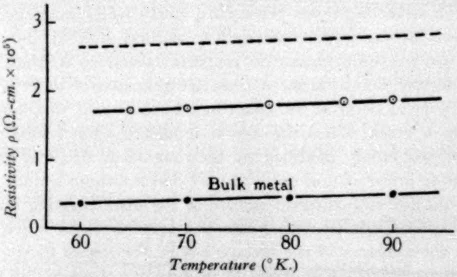


Figure 5. Theoretical - - -, and experimental ⊙. Resistivity/temperature graphs for a film 49·5 A. thick deposited at 64° K. ● bulk metal.

[*By the courtesy of the Royal Society*

The broken curve in figure 4 is obtained by substitution in formula (1), and it will be seen that there is good agreement between the theoretical and the experimental curves. This is all the more satisfactory since formula (1) contains no adjustable constants, but yields at once absolute values of the resistivity. The worst disagreement occurs precisely where we might expect; where the film is so thin that it cannot be expected to show the properties of a regular lattice, that is, at less than 10 A., or two crystalline layers, and at large thicknesses where t becomes comparable with λ_θ.

Rubidium and potassium also show good agreement at thicknesses greater than 30 A., though here it must be remembered that the decay process previously mentioned tends to raise the resistance above the theoretical value since even at 64° K. the first layers put down are disintegrating appreciably.

The temperature dependence of resistivity of the stable films may also be calculated from formula (1), and figure 5 shows a comparison of the results for caesium films 49·5 A. thick deposited at 64° K. It will be seen that they show a positive temperature coefficient.*

There seems little doubt that the explanation put forward above is correct in its broad features, but it is unlikely that the extremely simple assumptions put forward above are entirely correct. Calculations of a formula to replace equation (1) under more general conditions are at present being carried out by Fuchs.

§ 6. DISINTEGRATION OF THE FILMS. THE PHENOMENON OF DECAY

In references (6) and (7) a hypothesis is suggested which explains qualitatively all the phenomena of decay. The view put forward there was that the film was slowly tearing itself up under the influence of surface tension forces which in the thinner films may reach very high values; in a rubidium drop of radius 10 A. the pressure is of the order of 30 tons per square inch,† which is of the same order of magnitude as the ultimate tensile strength of carbon steel. Thus if a slice of an alkali metal could by some means be prepared about 10 A. thick it would immediately disintegrate if any cracks or imperfections existed at any point, because of the low elastic yield point of the alkali metals combined with the high stresses around any hole or crack. When the film is deposited upon a substrate the forces will however be profoundly modified by the magnitude of the surface energy at the metal-substrate interface and the film may become more stable.

Let us take a crude and concrete picture of the disintegrating film as a homogeneous metallic phase riddled with cracks and imperfections which are gradually widening under the influence of the surface forces. We regard these cracks as insulating barriers, the current being carried by bridges of unbroken film which become fewer and narrower as the disintegration proceeds. Assume that the continuous parts of the film are still thin compared with their linear dimensions measured along the surface. Then if E_1 is the surface energy of a free metal surface (necessarily positive) and E_2 is the (negative) surface energy at the metal-glass interface, it is clear that, fixing attention upon a definite geometrical configuration of the disintegrating film, the forces tending to disintegrate it further will be proportional to E_1+E_2. If E_1+E_2 is positive, as appears to be the case in these experiments, the film will continue to shrink away from the cracks, and to thicken up in the parts which remain intact until the curvatures at the free edges have enlarged so much that the surface tension forces can no longer cause flow in the metal. It is conceivable that this flow also produces a violent cold working of the crystals which hardens them and also gives rise to a *Restwiderstand.*

---

* The negative temperature coefficient observed in many early thin films is not explicable upon any simple theory of metallic conduction. It is indeed clear that no form of mere geometrical disintegration of the film (sponginess, porosity, etc.) can give a negative coefficient to a film if the bulk metal has the normal positive coefficient. The most that can happen is that the part of the resistivity due to strain in the lattice, and collision of the conduction electrons with the boundary, may swamp the temperature-dependent part to give a zero coefficient. Hence one may incline to the belief that perhaps septa of occluded gas between the crystals may account both for the negative temperature coefficient and the high specific resistance of such films. Even those prepared in vacuo classed as good by ordinary standards (tungsten(2), molybdenum(13)) cannot be guaranteed free from gas. Septa of gas have been suggested by Johnson and Starkey(14) to account for the high resistivity of certain mercury films.

† Drops as small as this contain relatively few atoms, so that the calculation is only correct as regards order of magnitude.

The above simple view of the decay process accounts satisfactorily for most of the experimental facts in the case of the alkali metals investigated. It describes satisfactorily the diminished decay factor for films deposited at the lower temperatures. At the lower temperatures the mechanical rigidity of the metal is increased, and so the flow will not take place so quickly; also during the deposition when alkali metal atoms are being deposited on the bare glass the lower temperature will diminish the mobility of the atoms over the glass surface, and on this account too the formation of cracks will be hindered. It explains the fact that, all other things being equal, the decay factor diminishes as the thickness of the film increases in the case of rubidium and potassium. And what is perhaps most important it satisfactorily explains why a film which is stable when deposited at a low temperature remains stable when raised subsequently to a higher temperature. For, once a continuous film has been formed, surface tension forces can only act so as to diminish any surface irregularities which do exist. The effect upon the stability of the films of minute traces upon surface impurities on the substrate also is perfectly comprehensible, for it is well known that the surface forces of the type of E_2 are particularly sensitive to contamination of the surface. There is only one observation which is in serious disagreement with the suggested picture: the fact that in caesium there is a certain range of nominal thickness over which the decay *increases* with the thickness. This suggests that the conception of the metal as a homogeneous phase may need reconsideration, as is mentioned later.

Lovell's results (unpublished) for potassium, rubidium and caesium show that only in the case of caesium does the resistivity of thick films converge to the value given for the ordinary bulk metal. Both potassium and rubidium give values about double the bulk resistivity but unfortunately the results so far obtained for rubidium are not very reliable. In the case of potassium, however, the excess resistivity can be accounted for as a *Restwiderstand* due to strain. Some of this strain can be relieved by annealing at 90° K., and a similar, though much smaller strain seems to exist in the thick layers of caesium.

Fuchs has compared the results now available for caesium, which extend from 0 to 12,000 A. with a more general theoretical expression than that previously used. The comparison seems to show that the assumption of inelastic scattering of the conduction electrons at the boundaries holds for the thinner films ($t/\lambda<1/100$) but that at greater thicknesses a considerable proportion of elastic scattering occurs.

Details of these calculations and of the comparison will be published elsewhere in the near future.

§ 7. AGGREGATION IN OTHER METAL FILMS

The idea that agglomeration of the metal might be responsible for the unusually high, or even infinite resistance of thin layers is not new; and its existence has received definite experimental proof in a large number of cases. We may quote, among others, the observations of Estermann(15) (ultra-microscopic examination of thin silver films), Fukuroi(16) (mercury, cadmium and zinc films deposited at 90° K. Optical evidence for agglomeration), Reinders and Hamburger(2) (silver deposited at room temperatures), Cosslett(17) (indium at liquid air temperatures), Andrade and Martindale(18) (sputtered silver films heated subsequently to about 600° K.). But in all previous work, except the last mentioned, the agglomeration has either been rapid and complete so that its intermediate stages could not be observed, or where resistance measurements were also attempted the structure of the films may have been marred by so many other extraneous factors that the primary role of the agglomeration process was obscured. The interest of these experiments on the alkali metals is that the process can apparently be followed in slow motion and under complete control. Moreover, the observation that mere alteration of the surface condition of the substrate without any other change in the experimental conditions can alter the specific resistance of the films by factors of 10^5 or more certainly suggests that the differing results of previous workers may be explicable in terms of a greater or less degree of agglomeration of their films. In fact, we may make the reasonable hypothesis that in all those cases where no electrical conductivity occurs until several atomic layers have been deposited a grained structure is responsible, the agglomeration in these cases being so rapid that with ordinary rates of evaporation no continuous film can be formed in the early stages of the process.

Various other hypotheses have been made to explain the experimental facts. Perucca(19), for example, suggests that all normal metals show anomalously high resistivity in the neighbourhood of a free surface. Thin films would thus show an abnormally high resistance owing to their large surface compared with their volume. There is no theoretical warrant for this belief, and no other experimental evidence to support it.

Zahn and Kramer(20, 21) similarly have proposed upon the basis of certain experimental results that an amorphous non-conducting layer of metal may be put down under certain circumstances. Their experimental results are certainly striking; but again, there is no experimental reason to suppose that thin metallic films are ever amorphous except in the case of antimony, and even if the films were amorphous, they would presumably show no higher resistivity than that of a melted metal.

It seems preferable on this account to exhaust the possibilities of the agglomeration hypothesis before looking elsewhere; and the following remarks tend to show that it may play an important role even at very low temperatures of deposition.

When we attempt to apply to other metals the simple picture already advanced to explain the alkalis, the immediate objection arises that nothing is known of the nature and hence the magnitude of the surface energy E_2, and that therefore the onus of explaining any experimental result can always be thrown upon E_2. We can overcome this objection to some extent, and incidentally get a somewhat clearer picture of the process of formation of evaporated films, by examining in closer detail the processes which take place in putting down the early atomic layers upon the substrate.

Let us first examine from a purely energetic point of view whether or not a layer of atoms approximately monomolecular would be inherently stable. Imagine two possible configurations of the metal upon the substrate. In the first (I) the atoms are supposed to be uniformly dispersed on the substrate; in the second (II) they are gathered up into a globule or agglomerate of small surface. Let L be the latent heat of evaporation of a metal atom from the surface, in electron volts, and L_{metal} the latent heat of evaporation from the metal. Then if $L < L_{\text{metal}}$ the state II or agglomerated form is the one with the lower energy. If $L > L_{\text{metal}}$ state I or the dispersed form has the lower energy. Thus a monolayer will be inherently stable if $L > L_{\text{metal}}$ and inherently unstable if $L < L_{\text{metal}}$.*

Now values for the latent heat of evaporation of metals from glass surfaces have been obtained in a few cases. Examples are given in the table below:

Table 2

Experimenter	Metal and surface	L (k.cal./g. atom)	L (eV.)	L_{metal} (k.cal./g. atom)	L_{metal} (eV.)
Estermann⁽²³⁾	Cd on glass	3·5	0·152	28	1·21
,,	Cd on Cu	3·0	0·130	28	1·21
,,	Cd on Ag	5·0	0·217	28	1·21
,,	Hg on Ag	2·5	0·109	18·5	0·80
Cockcroft⁽²⁴⁾	Cd on Cu Cd on Ag	5·7	0·247	28	1·21

The values of L given above represent the heat of evaporation of an atom from a dilute layer plus the heat of dissociation of a doublet upon the surface. L is therefore an upper limit for the latent heat of evaporation from a dilute layer. In all the above cases L_{metal} is about seven times larger than L and the agglomeration of a dilute layer is energetically possible. Now we were considering the general case of a layer which may approach monomolecular thickness. Although it is true that L will vary with the concentration of the layer it is unlikely that it can increase much† with θ (the fraction covered) and it is practically impossible that it should increase by a factor of seven. So a layer of any concentration will be energetically unstable.

The alkalis on clean glass have not yet been systematically investigated from this point of view. But the observation of Ives⁽²⁷⁾ and the experiments of Lovell⁽²⁸⁾ show that a clean glass surface placed in an evacuated enclosure filled with the saturated vapour of the alkali metals rapidly becomes coated with an invisible conducting layer of alkali metal which persists even though the glass is raised in temperature above its surroundings. The layer must be nearly monomolecular to conduct at all; and it follows that either the latent heat of evaporation of an atom of the alkali from the glass is greater than its heat of evaporation from the metal surface, in which case the glass will be completely covered, or, if less, L cannot differ from L_{metal} by more than a few kT., that is to say, by more than a few hundredths of an electron volt.

---

* De Boer⁽²²⁾ has previously pointed out that a high latent heat of evaporation for the adsorbed substance in bulk will favour agglomeration.

† Langmuir and Taylor⁽²⁵⁾ find that the latent heat of evaporation of neutral atoms from the surface actually falls from 2·83 volts at $\theta = 0$ to 1·77 volts at $\theta = 1$. J. K. Roberts⁽²⁶⁾ (H on W) shows that in this case the latent heat may somewhat more than double from $\theta = 0$ to $\theta = 1$.

It follows that the excess of energy of a dispersed layer over its agglomerated form is either small or is actually negative, and for this reason alone single layers of alkali metal atoms on glass should be more stable than those of cadmium or mercury on the surfaces investigated by Estermann and Cockcroft.

So far we have only discussed whether the agglomeration is energetically possible. Whether it will also in fact take place depends upon the mobility of the atoms over the surface of the glass. Lennard-Jones(29) has given a simple picture of the chief factors which influence this mobility, and we may apply it to the present case.

According to his model an atom on a surface may be regarded as held there by a field of force which has a certain potential. The equipotentials are not however a series of planes parallel to the surface, as we have tacitly assumed till now; a crystal surface, for example, has a periodic structure. On this account regular pockets of low potential will exist upon the surface, and at low temperatures any deposited atoms will vibrate about the minima of these pockets. The latent heat of evaporation of the atom from the surface will then be the energy required to remove an atom from its lowest vibrational level to infinity. But in order to move freely over the surface an atom needs much less kinetic energy than L. In fact, if the atom is given sufficient kinetic energy A for it to surmount the potential barrier between one pocket and the next, it may (so long as it retains the energy) move freely over the surface. Thus, since A is less than L, free motion of the atoms on the surface occurs at temperatures far below those needed to evaporate the atoms from the surface: a well-known experimental fact.

Now A, like L, is dependent both on the nature of the surface and upon the atom concerned. It has been found for metal atoms in a limited number of cases only, and it depends to some extent upon the surface population of the atoms. But we may say in general that L and A increase together. Lennard-Jones(29) estimates that for the particular case of the inert gases upon a surface of alkaline halide A is about $\frac{1}{3}L$. Dilute layers of caesium on tungsten give an activation energy of 0·61 volt and a latent heat of 2·83 volts(25, 30). Bosworth(31) obtains values between 0·14 and 0·57 volt for sodium on tungsten, Frank(32) between 0·2 and 0·6 volt for caesium on tungstic oxide. The latent heats of evaporation of neutral atoms are not known in the latter case but they are certainly greater than 1 electron-volt. We might guess then that the activation energy of an atom on a surface is generally less than a third of the latent heat of evaporation from the surface and may be about a quarter.

On this basis the activation energy of caesium on glass must be at least 0·25 volt, whereas cadmium on glass, using Estermann's value for the latent heat, would have an activation energy of only 0·04 volt. This difference will be reflected in a great difference of mobility in the two cases. Assuming a time of activation of about 10^{-13} second (Lennard-Jones(29)) and a surface temperature of 90° K. in both cases we find that a caesium atom would be activated only once every ten seconds, when it would move a distance of 0·6 A., whereas a cadmium atom would be activated nearly 10^{11} times in one second, would move a total distance of about 200 cm., and would migrate about $\frac{1}{100}$ mm. from its original position in this time.

This estimate is purely illustrative and it is of course very sensitive to the actual values of the activation energy assumed. Nevertheless it does enable us to understand how it may be possible in the case of the alkalis to lay down a second layer of atoms before the atoms in the first layer have moved much from their original positions, whereas in the case of cadmium at the same temperatures rates of deposition quite impracticably rapid would have to be used to do this.

We might therefore classify metallic films into three broad classes depending upon the stability of their first layers. For type I, $L > L_{\text{metal}}$ and the first layer is inherently stable. The classical example of this is caesium atoms on clean tungsten for all values of θ. Perhaps caesium on clean glass also belongs to this group; for this would account for the great stability of the early layers in the experiments we have already described using this particular metal. For type II, $L < L_{\text{metal}}$ but $L \sim 1$ electron volt or more. The activation energy is a few tenths of a volt, agglomeration takes a period of minutes at 90° K. and fairly coherent films can be readily prepared at somewhat lower temperatures of deposition, using deposition rates of the order of a molecular layer in a few minutes. For type III $L < L_{\text{metal}}$, $L \sim 0{\cdot}1$ eV. and the activation energy is only a few hundredths of an electron volt.* Films of type III will show rapid agglomeration even at very low temperatures of deposition and in fact approximate to the two-dimensional gas of Frenkel(33) and Cockcroft(24). These metals even when deposited at very low temperatures will show very different resistivity-thickness relations from the alkalis. We may imagine the successive stages in the development of a film of this type somewhat as follows, starting from the bare substrate: As deposition proceeds doublets are first formed which gradually accrete more atoms round them, and island patches of metal are formed. During this stage of the process there can be no electrical conductivity since the film consists of flat isolated aggregates joined only by a very dilute phase of two-dimensional gas. As the deposition proceeds the island patches thicken both from condensation at their free surfaces and by shrinking under their very high surface-tension forces. The next stage in the process occurs when the aggregates have become so thick and the curvatures of their free surfaces have been so diminished that the surface forces can produce no further flow in the metal. The aggregates now thicken only slowly from deposition at their upper faces, and continue to grow edgewise by condensation from the two-dimensional gas. At a certain stage they will touch, and conductivity will abruptly begin. After this the film-resistivity should quickly approximate to that of the bulk metal.

Some preliminary results obtained in this laboratory with thin films of mercury-on-pyrex certainly suggest that these films are an extreme form of type III even when the deposition takes place at temperatures as low as 20° K. Figure 6 shows a family of {resistivity, thickness} curves, each curve characteristic of a different temperature of the condensing surface. (Deposition rate about 9 A./min. in all cases, but this is subject to correction on calibrating the beam, a difficult matter in the case of mercury). The short vertical marks above each curve show the onset of conductivity. This was remarkably sudden, the resistance falling from an unmeasurably high value greater than 10^{10} ohms to a few thousand ohms within about 15 sec., which corresponded to an increase in nominal thickness of less than a monolayer. At this point in the deposition, when the aggregates first touched, the film rapidly disintegrated if currents greater than a few microamps passed through it.

---

* Semenoff, Chariton, and Schalnikoff(38) have discussed films of type III from a similar point of view to the above, without reference however to the effect on the electrical conductivity.

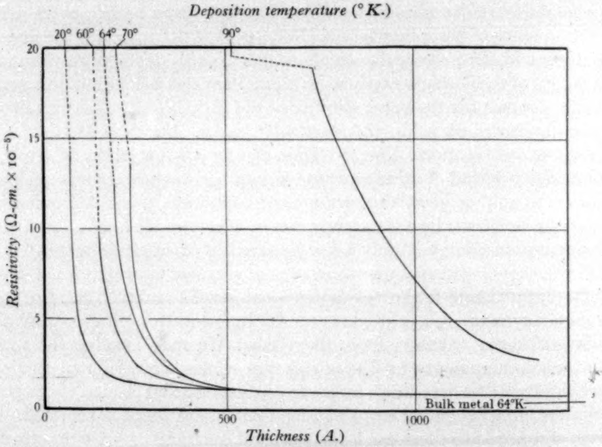


Figure 6.

Figure 7 shows critical thickness plotted against deposition temperature. It will be noticed that there appear to be no signs that by lowering the temperature below 20° K. the critical thickness will much diminish. Thus there appears the surprising suggestion that apparently the atoms of mercury retain their mobility down to very low temperatures. Mercury atoms on pyrex therefore may be similar to helium atoms on lithium fluoride which, according to the theoretical calculations of Lennard-Jones(34), have a finite mobility at all temperatures above absolute zero.

On our picture of the process we should estimate that the critical thickness of the film is about the thickness of an aggregate whose curvatures have so diminished that the surface forces can no longer produce any plastic deformation. Now roughly speaking the stresses due to surface forces in an aggregate are inversely proportional to its thickness. The critical thickness should therefore give us a measure of the weakness of the metal at that temperature. Although no experiments appear to have been done on single crystals of mercury at these low temperatures, a rough comparison with the results for magnesium(35) single crystals suggests that mercury, which has a low melting point, might begin to alter its mechanical properties rapidly in the region of 80° K., where the rapid rise of critical thickness with temperature does set in. But until further evidence accumulates we must regard this as a speculative guess, particularly since all experiments on the mechanical properties of metal crystals have been carried out with large specimens and not with the microscopic or submicroscope aggregates we have postulated in thin films.

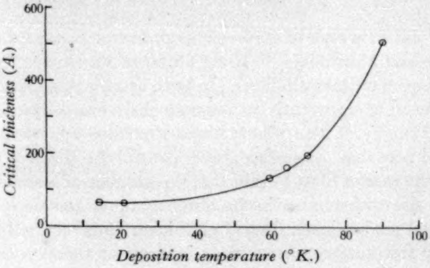


Figure 7.

To summarize the above conclusions: The foregoing discussion suggests that the degree of agglomeration in evaporated films is determined on the one hand by the activation energy of the atom upon its substrate, on the other by the resistance of the metal to plastic deformation, not simply by the melting point of the metal as certain writers have suggested.

§ 8. RECRYSTALLIZATION OF THIN METAL FILMS

Films which agglomerate in their early stages must have a very finely polycrystalline structure which may persist to great thicknesses. The resultant large surface of misfit between the microcrystals may have two effects. First they may increase the resistance of even thick films appreciably above that of the bulk metal; secondly, they introduce a new type of surface energy which may become important when their area becomes large compared with that of the boundaries of the film.

The effect on the resistivity of the film would be to add a *restwiderstand* to the normal resistivity, and on this account even very thick evaporated films deposited at temperatures below that at which recrystallization would occur might show a considerable excess of resistivity over that of the normal metal. It seems possible that in most of the cases where this resistivity excess does not exceed the increase of resistivity on melting for the pure metal, it may be due to this cause. Annealing should then diminish the resistivity of the films by allowing the surfaces of misfit to relax (recrystallization).

The experiments of Suhrmann and Barth(36) on thick films of copper deposited at 20° K. are consistent with this hypothesis. Annealing at successively higher temperatures lowered their resistivity by diminishing the *restwiderstand* without altering the resistivity change between two definite (lower) temperatures. The highest resistivities observed were nevertheless somewhat in excess of the resistivity change of copper on melting, and it seems on this account possible that occluded gas may have introduced a disorder in the lattice exceeding that produced by melting. Wand(37) has worked out a theory of the relaxation of strain in the lattice which is consistent with his own experimental results, and further experimental work on this point would be valuable.

The effect of this new type of surface energy may account too for the observations of Andrade and Martindale(18) (silver films) as also some recent unpublished observations of Lovell on caesium films. In both cases it was found that thick films could disintegrate so as apparently to increase their free surface and hence their ordinary surface energy. These observations therefore apparently contradict the ideas put forward here that the surface forces control the shape of the film. It is in fact true that in the case of films so thin that the number of atoms in the surfaces is comparable with the total number in the film (say up to 20 atomic layers) ordinary surface forces must predominate. But when thicker films recrystallize it is not at all unlikely that the free-surface energy may increase at the expense of the energy gained from recrystallization and relaxation of the surfaces of misfit.

§9. ACKNOWLEDGEMENTS

I wish to express my thanks to Dr Lovell and Dr Fuchs for permission to publish the preliminary account of their results.

I am also indebted to the Royal Society for permission to reproduce figures 2, 3, 4, and 5 of the present paper (which were originally published in their *Proceedings*) and for the loan of the blocks.

REFERENCES

(1) Bartlett. *Phil. Mag.* **5**, 848 (1928).
(2) Reinders and Hamburger. *Rec. Trav. chim. Pays-Bas*, **50**, 441 (1931).
(3) Vincent. *Ann. Chim.* (*Phys.*), (8), **9**, 433 (1900).
(4) Pogany. *Ann. Phys.*, Lpz., **49**, 531 (1916).
(5) Weber and Oesterhuis. *Proc. Acad.*, Amsterdam, **25**, 606 (1916).
(6) Lovell. *Proc. roy. Soc.* A, **157**, 311 (1936).
(7) Appleyard and Lovell. *Proc. roy. Soc.* A, **158**, 718 (1937).
(8) Thomson. *Proc. Camb. Phil. Soc.* **11**, 119 (1901).
(9) Hamburger. *Ann. Phys.*, Lpz., **10**, 796 (1931).
(10) Wood. *Phys. Rev.* **44**, 353 (1933).
(11) Zener. *Nature*, Lond., **132**, 968 (1933).

(12) Mott and Zener. *Proc. Camb. Phil. Soc.* **30**, 249 (1934).
(13) de Boer and Kraak. *Rec. Trav. chim. Pays-Bas*, **55**, 941 (1936).
(14) Johnson and Starkey. *Proc. roy. Soc.* A, **140**, 126 (1933).
(15) Estermann. *Z. phys. Chem.* **106**, 403 (1923).
(16) Fukuroi. *Honda Anniversary Volume*, p. 80 (1936).
(17) Cosslett. *Proc. phys. Soc.* **49**, 121 (1937).
(18) Andrade and Martindale. *Philos. Trans.* **235**, 69 (1935).
(19) Perucca. *Ann. Phys.*, Lpz., **4**, 252 (1930).
(20) Zahn and Kramer. *Z. Phys.* **86**, 413 (1933).
(21) Kramer. *Ann. Phys.*, Lpz., **19**, 37 (1934).
(22) de Boer. *Electron Emission and Adsorption Phenomena*, p. 48 (1935).
(23) Estermann. *Z. Phys.* **33**, 320 (1925).
(24) Cockcroft. *Proc. roy. Soc.* A, **119**, 293 (1928).
(25) Langmuir and Taylor. *Phys. Rev.* **44**, 423 (1933).
(26) Roberts. *Proc. roy. Soc.* A, **152**, 445 (1935).
(27) Ives and Johnsrud. *Astr. J.* **62**, 309 (1925).
(28) Lovell. *Proc. phys. Soc.* **49**, 89 (1937).
(29) Lennard-Jones. *Trans. Faraday Soc.* **38**, 333 (1932).
(30) Langmuir and Taylor. *Phys. Rev.* **40**, 463 (1932).
(31) Bosworth. *Proc. roy. Soc.* A, **150**, 58 (1935).
(32) Frank. *Trans. Faraday Soc.* **32**, 1403 (1936).
(33) Frenkel. *Z. Phys.* **26**, 117 (1924).
(34) Lennard-Jones and Devonshire. *Proc. roy. Soc.* A, **158**, 242 (1937).
(35) Schmid and Boas. *Krystallplastizität*, p. 160 (1935).
(36) Suhrmann and Barth. *Z. Phys.* **103**, 133 (1936).
(37) Wand. *Z. Phys.* **104**, 1 (1937).
(38) Semenoff, Chariton and Schalnikoff. *Trans. Faraday Soc.* **28**, 169 (1932).

A STUDY OF THE ELECTRICAL PROPERTIES OF THIN FILMS OF PLATINUM OBTAINED BY CATHODE SPUTTERING IN AIR AND OTHER GASES (He, N_2, O_2 AND H_2)

By A. FÉRY, Collège de France, Paris

For a considerable time attempts have been made to use cathode sputtering in order to obtain thin metallic films so as to study, in particular, the variation of resistivity of these films as a function of their thickness.

All investigators agreed that up to a certain so-called critical thickness the resistivity of the films is a diminishing function of the thickness. Beyond the critical thickness the metal has quite definite physical properties which are those of the *bulk* metal. But for platinum, for example, there are notable discrepancies between the values obtained by different investigators, both for the resistivity of these films at one and the same thickness, and also for the values of the critical thickness. Moreover the resistances obtained in this way were in no way permanent; the adsorption of gas atoms seems to be important. The same uncertainty existed for the temperature coefficients.

I therefore thought that it would be interesting to take up once again the study of the electrical resistance of thin platinum films, with the primary object of getting stable resistances, using first a discharge in air. By taking the same precautions employed in the manufacture of radio valves and, in particular, by getting rid of all traces of water vapour from the apparatus before sputtering (by baking-out in a high vacuum) I was successful in achieving this. The deposits were kept in the apparatus throughout their life. But the platinum so obtained is not ordinary platinum as we shall see in what follows. We shall call it *black platinum*.

I was thus enabled to determine the experimental relationship between the resistivity ρ and the thickness l of these black platinum films. This relationship, which holds between 10 mμ. and 1320 mμ. may be divided into the two curves

$$2 \log (\rho/\rho_0) = 11{\cdot}48 - 0{\cdot}0315\, l$$

and

$$2 \log (\rho/\rho_0) = 3{\cdot}245,$$

where $\rho_0 = 10^{-5}$ ohm-cm. which is the average resistivity of ordinary platinum. These curves are joined up between 237 and 285 mμ. by a very short curved line.

Beyond 285 mμ. the metal may therefore be taken to be compact. But it is nevertheless not ordinary platinum: its resistivity ($4{\cdot}19 \times 10^{-4}$ ohm-cm.) is 42 times higher than the average resistance of bulk platinum. Moreover it appears black. This kind of platinum is adsorbent, has a high resistance, and is catalytic.

Throughout these experiments the temperature of the plate upon which the deposit was received did not increase during the passage of the discharge, for the voltage was low. But if the deposits are heated *in vacuo* their resistance changes. It first increases *reversibly* as the temperature rises, then as soon as the temperature reaches a certain threshold the resistance alters very rapidly and irreversibly, at constant temperature. It diminishes continuously, tending towards a certain limit depending on the temperature of the threshold. By again raising the temperature the same phenomena are reproduced. One thus obtains a series of reproducible transition points 53°, 83°, 97°, 114°, 241° and 340° C. Only at 340° C. do the films have a resistivity between the limits of the tabulated values for normal platinum.

Between any two successive transition temperatures the deposit has quite clearly defined properties. The temperature-coefficient in particular which was $2{\cdot}87 \times 10^{-4}$ for black platinum increases as one approaches the normal bulk metal and finally takes the value $29{\cdot}9 \times 10^{-4}$ very close to that given for the normal metal.

If sputtering is carried out without taking these precautions to avoid heating of the substrate, the form of deposit stable at the temperature reached by the substrate is obtained. This explains the great divergence of the previous results.

The transitions are accompanied by very slight evolution of gas at the first three transition points (the least noteworthy ones). But this evolution of gas is due only to a small adsorption by the deposits (oxygen, nitrogen and oxides of nitrogen) during or after their formation; an adsorption so slight that it can only play a very secondary role in the development of their physical properties.

After transformation into white platinum a new curve is obtained relative to normal platinum. The critical thickness is considerably diminished. It occurs in the neighbourhood of 50 mμ. The "compact" metal has then the resistivity of ordinary platinum. But at very small thicknesses (between 3 and 6 mμ.) this curve is observed to appear to join up again with that of black platinum. The two forms then become indistinguishable.

The properties of the deposits obtained in the simple gases (helium, nitrogen, oxygen, hydrogen) are not clearly defined. During their formation these deposits absorb the gas of the discharge.

At ordinary temperatures after their preparation their resistances fall and tend towards a limit. On heating and holding the temperature at an arbitrarily chosen value, their resistance diminishes again at constant temperature, approaching a new limiting value which is a function of the constant temperature. Parallel with this process the occluded gases are released at a rate which increases the more the temperature is raised. At 500° C. we have still not been able to obtain normal platinum, and the films so obtained are torn up by the evolution of the absorbed gas.

FLUCTUATIONS IN THE RESISTANCE OF THIN FILMS

J. BERNAMONT, Collège de France, Paris

THE study of fluctuations of resistance, begun in 1934(1), has been pursued up to the present time with deposits of graphite(2), with microphone(3) and with metallic deposits(4). The general results obtained are the following: the mean square of electromotive force averaged over a complete period, which we denote by $\overline{e_\nu^2}$, is approximately proportional to the square of the intensity of the current carried by the conductor, at least in the range of frequencies studied. This range is at present too restricted to allow general conclusions to be drawn; in the experiments with metallic deposits it extends from 96 to 162,000 hertz, while other authors have limited themselves to frequencies from 50 to 10,000. The mathematical investigation of the fluctuations(4) makes it possible to predict that for sufficiently low frequencies $\overline{e_\nu^2}$ ought to be independent of the frequency, and for high frequencies $\overline{e_\nu^2}$ ought to diminish at least as fast as $1/\nu^2$. The curve showing $\log \overline{e_\nu^2}$ as a function of $\log \nu$ ought then to be made up of at least three branches of very different slope, viz. (*a*) a horizontal part for low frequencies; (*b*) for intermediate frequencies a part about which nothing can at present be said from the theoretical point of view, but for which experiment gives a slope of 1; (*c*) for high frequencies a branch with a strong negative slope (at least -2).

The branch (*c*) has been observed with a tungsten deposit;(4) the slope was exactly -2 from 72,000 to 162,000 hertz(4). Experiments on graphite and microphone(2) show some indications of (*a*).

Since my first observations I have held the opinion that this fluctuation was due to fluctuations in the number of free electrons in the conductor which would give rise to fluctuations in the resistance. A variable electromotive force ought then to appear in the circuit, whose mean square is given by the formula

$$\overline{e^2} = I^2 \overline{\Delta R^2},$$

where ΔR is the instantaneous deviation of the resistance from the mean value.

On the classical theory one can deduce for a cylindrical conductor

$$\overline{e^2} = (I^2 R^2 / n_0 a)\, \overline{\Delta N^2} / N.$$

M. L. Brillouin(5) has shown that this formula follows also from quantum statistics; but the factor $\overline{\Delta N^2}/N$ which is independent of the volume is equal to 1 according to the classical theory but can have another value according to the quantum theory.

To obtain the dependence of $\overline{e^2}$ on ν, one must make a more detailed hypothesis about the mechanism. I have assumed that a free electron has a mean life-time

$\theta=1/\alpha$. Its collisions with atoms will only alter the direction of its velocity v; and it is only after a very large number of collisions that the electron is captured by an atom and ceases to be free. A group of n free electrons may thus be reduced in number to $ne^{-\alpha t}$ at the end of a time t. Naturally other electrons will be liberated at random during the same interval; this hypothesis leads to the formula

$$\overline{e_\nu^2}=I^2R^2\frac{\overline{\Delta N^2}}{N}\frac{4\alpha}{\alpha^2+4\pi^2\nu^2}.$$

This equation is not in agreement with experiment; but we need not assume that electrons of different velocities have the same life time. If dn is the number of electrons for which the constant α lies in the range $d\alpha$, and if we write

$$\overline{\Delta dn^2}/dn=g$$

then we obtain finally

$$\overline{e_\nu^2}=\frac{I^2R^2}{n_0^2\,\alpha}\int_{\alpha_1}^{\alpha_2}\frac{4\alpha g\,dn}{\alpha^2+4\pi^2\nu^2},$$

where α_1 and α_2 are the limiting values of α. This formula reproduces the branches (*a*) and (*c*) very well.

Comparison with the experimental branch (*b*) gives us αg as a function of v (for dn is a function of v). But definite conclusions on this subject would be premature.

Actually all experiments of this type have been carried out on conductors of rather badly defined nature. The platinum films have been obtained by M. Féry's method and were very thin. Their thickness was about 40 A., and in M. Féry's experiments conduction only began at 31 A. As one does not know the reason for the absence of conductivity for thinner films the results are rather hard to interpret. It would be desirable to repeat the experiments with films obtained by the method of Appleyard and Lovell and also perhaps with semi-conductors, in such a way as to avoid perturbations which can occur at the contacts where the current enters the film.

REFERENCES

(1) Bernamont, J. *C.R. Acad. Sci., Paris*, **198**, 1755, 2144 (1934).

(2) Meyer, E. and Chiede, H. *Elekt. Nachr.-Tech.* **12**, 237 (1935).

(3) Christensen, C. J. and Pearson, G. L. *Bell Syst. tech. J.* **15**, 197 (1936).

(4) Bernamont, J. Thèse de doctorat, Paris, and *Ann. Phys., Lpz.*, **7**, 71 (1937).

(5) Brillouin, L. *Helv. phys. Acta*, **7**, 47 (1934).

THE MIGRATION AND AGGREGATION OF ATOMS ON SOLID SURFACES

By J. E. LENNARD-JONES, University Chemical Laboratory, Cambridge

§ 1. INTRODUCTION

The interesting experiments of Appleyard and Lovell(1) on the electrical properties of thin films of the alkali metals on pyrex glass direct attention to a number of important theoretical problems concerning the properties of atoms deposited on surfaces. Appleyard* has suggested that when in his experiments a clean surface is bombarded uniformly by metallic atoms, their subsequent behaviour will be conditioned by the surface field of the substratum and by the relative magnitudes of the heat of evaporation from the surface and the heat of sublimation of the metallic atoms from the bulk phase. If the forces of the substratum are strong enough, the metallic atoms may be held in a continuous (more or less uniform) two-dimensional film and its electrical resistance is then of the same order of magnitude as that of the bulk metal. If, however, the cohesive forces between the metal atoms themselves are stronger than those of the substratum, the metallic atoms may tend to aggregate into "islands", which may be many atoms thick. This tendency to aggregation will be opposed by the periodic nature of the surface field and the time taken for the film to reach its most stable configuration will be governed by the rate at which the atoms can migrate over the surface.

This qualitative picture suggests a theoretical investigation of the behaviour of an atom, deposited on a surface, in terms of the interatomic forces between the atoms themselves and between each atom and the surface. The first problem is to determine what is the most stable configuration of the atoms thus deposited. It may be that of a uniform two-dimensional film, or a number of two-dimensional aggregates. On the other hand small three-dimensional crystallites may be more stable than either. This problem is a thermodynamic or statistical one and the answer to it will give the configuration which will eventually be reached after the lapse of a sufficiently long time. In the actual experiments the atoms are deposited uniformly and may or may not be in the configuration which is most stable. The next problem is therefore a dynamic one and is concerned with the length of time it will take the assembly to change from its initial configuration to the most stable one. This will depend on the rate at which atoms can surmount the energy barriers of the periodic field at the surface(2). In this paper we shall consider some aspects of these two problems.

---

* The author is greatly indebted to Dr Appleyard for an advance copy of his paper to this conference, with its valuable review of the experimental facts.

§ 2. CRITICAL PHENOMENA IN ADSORBED FILMS

The experiments of Cockcroft(3) and others have shown that when metals are deposited on a surface, they form condensed films if the temperature of the surface is less than a certain critical value. The behaviour of atoms adsorbed on a surface is, in fact, somewhat similar to that of gases and vapours, all of which exhibit critical properties below a certain temperature.

The existence of these critical conditions was discussed by Frenkel(4) who considered the formation of doublets on a surface, held together by an energy greater than that binding them to the surface. He showed that under these conditions a dispersed layer of single atoms would become unstable below certain critical conditions and condensation would occur.

Fowler(5) has recently made a new approach to the problem, basing his work on the treatment of order-disorder phenomena in alloys by Bragg and Williams(6) and Bethe(7). The energy of an adsorbed atom is assumed to depend not only on the attraction of the surface but also on the number of nearest neighbouring sites occupied by other adsorbed atoms. The assumption was made that the energy of adsorption was a linear function of the number of nearest neighbours. Peierls(8) has shown the relation of Fowler's treatment to Bethe's method and has obtained the critical conditions for atoms adsorbed on a surface when the number of nearest neighbours has any value, Fowler's results being a special case of his.

It may be of interest to give another method of arriving at similar results. We suppose a number of atoms deposited on a perfectly plane surface. At high temperatures and low concentrations these will behave like a two-dimensional gas and binary encounters will alone be of importance. The potential energy of any one atom, referred to an atom at rest in the gas phase as zero, will then be given by

$$\chi = \chi_0 + \nu \int_0^\infty \chi_1 e^{-\chi_1/kT}\, 2\pi r\, dr \qquad \ldots\ldots(1),$$

where χ_0 is the heat of adsorption of an isolated atom, and χ_1 is the potential energy between any two atoms; ν is the concentration of atoms and is related to θ, the fraction covered by $\theta = \nu S$, where S is the area of each cell into which the surface may be regarded as divided. We see that the equation (1) is similar to the form assumed by Fowler, except that the factor of θ is a function of temperature.

When the concentration becomes high (θ approaches unity), it will not be sufficient to take into account the interaction of pairs only. It will be necessary to calculate the potential of aggregates of atoms. Moreover it will be necessary to work out not only the critical conditions for a two-dimensional phase, but also for the case when the adsorbed atoms can condense together into three-dimensional groups. It is not yet known how the critical conditions for a two-dimensional assembly compare with those of a three-dimensional one. If the critical temperature for two dimensions is higher than that for three, two-dimensional groups may form before three-dimensional ones; but if the critical temperature for two dimensions is lower than that for three, the presumption is that two-dimensional groups will never form, or if they do, they will very quickly change to the more stable configuration.

An approximate answer to this problem may be obtained by means of a model. We consider a two-dimensional assembly on a perfectly smooth surface. At large densities each atom will always be the immediate neighbour of several others, each of which will exert forces on it and contribute to its potential energy. Although the atom may move from one part of the surface to another, it will always appear to be imprisoned by its environment and will make rapid vibrations about its average path. We may represent this state of affairs by supposing the atom confined to an area, constant in amount and equal to the average area available for each atom, and that within this area there is a region of constant potential energy. The average potential of an atom will, however, depend on the density of the assembly. It will be small for low densities and will gradually fall (to negative values) as the density increases, until a density is reached corresponding to that of a two-dimensional liquid or solid. After this the potential will rise if it is further compressed. So we suppose the potential within a cell to be a suitable function of the area so as to reproduce these features.

The partition function of an atom will then be

$$f = A\,\frac{2\pi m\,kT}{h^2}\,e^{-\chi(A)/kT}\,v_z(T) \qquad \text{......(2),}$$

where A is the area and $\chi(A)$ the potential in the cell, while $v_z(T)$ represents the contribution of the vibration perpendicular to the surface. We assume* that the partition function of the whole assembly can be written as f^N, where N is the number of atoms. Then the free energy of the assembly is

$$F = -NkT\log f \qquad \text{......(3),}$$

and the two-dimensional pressure P is given by

$$\begin{aligned} P &= NkT\left\{\frac{\partial}{\partial A}\log f\right\}_T \\ &= NkT\left\{\frac{1}{A} - \frac{\chi'(A)}{kT}\right\} \qquad \text{......(4).} \end{aligned}$$

The potential $\chi(A)$ has the required properties, if it be assumed that

$$\chi(A) = \frac{\lambda}{A^n} - \frac{\mu}{A^m} \qquad \text{......(5)}$$

with $n > m$.

The critical volume and temperature are given by

$$\left(\frac{\partial p}{\partial A}\right)_T = \left(\frac{\partial^2 p}{\partial A^2}\right)_T = 0 \qquad \text{......(6).}$$

These lead to the result that

$$kT_c = \alpha\,|\,\chi(A)\,|_{\max.} \qquad \text{......(7),}$$

where α is a pure number, given by

$$\alpha = m\,(m+1)\,[m\,(m+1)/n\,(n+1)]^{m/(n-m)} \qquad \text{......(8).}$$

---

* This step is discussed in a forthcoming paper by the author and A. F. Devonshire on critical phenomena in gases.

A similar result could clearly be obtained for a three-dimensional assembly, using similar methods, viz.

$$kT_c^* = \alpha^* \mid \chi^* (v) \mid_{\max.} \qquad \ldots\ldots(9),$$

where α^* is a similar function of numbers m' and n'. A more detailed and accurate calculation by the author and A. F. Devonshire(9) taking into account the variation of the field within a cell, so that χ is a function not only of v but also of the space coordinates, leads to a similar result for the three-dimensional case and it is found that for the inert gases

$$kT_c = (4/3) \mid \phi \mid_{\max.} \qquad \ldots\ldots(10),$$

where $\mid \phi \mid_{\max.}$ is the energy of dissociation of two atoms. Similar calculations are being made for two dimensions but, in the meantime, it may be said that the indication is that the critical temperature for two-dimensional condensation is lower than that for three dimensions.

The free energy for two dimensions is given by

$$F = -NkT \left\{ \log A + \log (2\pi mkT/h^2) - \frac{\chi(A)}{kT} + \log v_z(T) \right\} \qquad \ldots\ldots(11),$$

and that of a three-dimensional assembly is

$$F^* = -NkT \left\{ \log v + \tfrac{3}{2} \log (2\pi mkT/h^2) - \frac{\chi(v)}{kT} \right\} \qquad \ldots\ldots(12).$$

The difference of the free energies in the two phases is thus (for this model)

$$F^* - F = NkT \left\{ \log \frac{Av_z(T)}{v(2\pi mkT/h^2)^{\frac{1}{2}}} + \frac{\chi(v) - \chi(A)}{kT} \right\} \qquad \ldots\ldots(13).$$

If the potential energy of the adsorbed atom as a function of its distance from the adsorbing surface be represented by a region of constant potential χ_0 for a length z_0, when it changes discontinuously to zero, we get for v_z,

$$v_z = (2\pi mkT/h^2)^{\frac{1}{2}} z_0 e^{-\chi_0/kT} \qquad \ldots\ldots(14),$$

and then

$$F^* - F = NkT \left\{ \log \frac{Az_0}{v} + \frac{\chi(z) - \chi(A) - \chi_0}{kT} \right\} \qquad \ldots\ldots(15).$$

When the volume of an atom in the adsorbed phase Az_0 is comparable with the volume of an atom in the three-dimensional phase v, we see that F^* is less in absolute magnitude than F when

$$\chi(v) < \chi(A) + \chi_0.$$

Now each of the χ's is the potential energy of a "hole" and is negative, so that we have $\chi = -\mid \chi \mid$ and the condition can be written

$$\mid \chi(v) \mid > \mid \chi(A) \mid + \mid \chi_0 \mid \qquad \ldots\ldots(16).$$

The left hand side may be taken to be the heat of sublimation of the three-dimensional phase and $\mid \chi(A) \mid + \mid \chi_0 \mid$ the heat of adsorption from a condensed two-dimensional phase. This condition is the same as that discussed by Appleyard in his contribution to this discussion, but it is clear that it is only true when the contribution of the vibrational motion to the free energy takes the special form given to it in the above treatment.

The heat of sublimation of a metal is usually much greater than the heat of adsorption of the same metal on to another surface and three-dimensional aggregates are more likely than two-dimensional ones, but the experiments of Appleyard on alkali metals, deposited on pyrex glass, show that in some cases the two energies are comparable in value. For caesium deposited on tungsten special ionic forces are probably brought into play for the first layer owing to the transfer of an electron from an adsorbed atom to the underlying metal and then the two-dimensional phase is unusually stable. These same ionic forces will, however, reduce the value of $|\chi(A)|$ as the film becomes more condensed owing to the mutual repulsion of the dipoles created between caesium and tungsten and eventually $|\chi(v)|$ may be greater than $|\chi(A)|+|\chi_0|$.

§ 3. THE MIGRATION OF ATOMS ALONG SOLID SURFACES

The migration of atoms along solid surfaces has now been investigated by many workers. A summary of work up to 1932 was given by Volmer(10) and since then the technique of measuring the rate of migration has been developed by Langmuir(11), Becker(12), Bosworth(13), and others(14). In all cases the rate of diffusion is found to vary with temperature according to an exponential law, at any rate approximately, but sometimes, as in the case of caesium on tungsten, the rate of diffusion is also a function of the concentration of atoms in the surface phase.

A theory of surface migration was given by the author(2) in 1932. It was there pointed out that the field in which an atom moves near an adsorbing surface is not two-dimensional in character, as had often been assumed, but was undulatory with a double periodicity similar to that of the lattice. A section of a typical field is shown in figure 1. The continuous lines are sections of the surfaces of equal potential energy. In the immediate neighbourhood of the position of minimum energy the surfaces are closed but eventually they open out and consist of two branches, one above and one below the equilibrium positions.

At low temperatures an adsorbed atom will vibrate about one of the points where the potential energy is a minimum, but, as the temperature of the adsorbing solid is raised, the probability increases that the atom will receive sufficient energy to surmount the potential barrier separating one potential minimum from the next. In order that an adsorbed atom may migrate it must be activated sufficiently to pass over the col between two potential pockets. It was shown that if γ is the number of times per second that an atom is activated to this mobile state and l is the average distance travelled before it is deactivated, the coefficient of diffusion D, defined as usual by the equation

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2},$$

is given by

$$D=\alpha\gamma l^2 \qquad \text{......(17)},$$

where α is a certain numerical constant of the order of $\frac{1}{2}$ or $\frac{1}{4}$. If the average lateral velocity of an atom during activation is $\bar{v}$ and the average time it remains activated is τ, while τ^* is the average interval of time between successive activations of the same atom we may write alternatively

$$D = \alpha\bar{v}^2\tau^2/(\tau+\tau^*) \qquad \text{......(18}a\text{)},$$

and if, as in many cases, τ^* is very long compared with τ, we may write

$$D = \alpha\bar{v}^2\tau^2/\tau^* \qquad \text{......(18}b\text{)}.$$

Once D is known from theory or experiment, the bulk diffusion can be calculated by the usual methods (2).

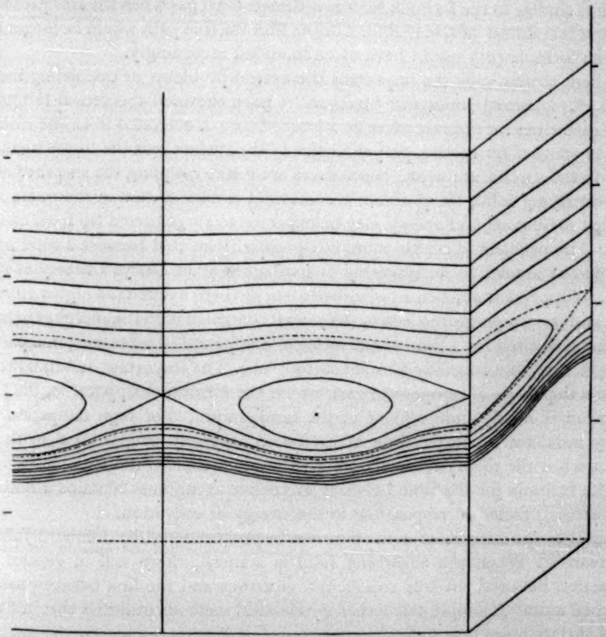


Figure 1. Two cross-sections of the potential field near an adsorbing surface. Continuous lines are sections of equipotential surfaces.

Langmuir in a later paper (11b) gave a special case of (18b), based on the assumption that an adsorbed atom is surrounded by four neighbouring sites and that an activated atom hops only to one of them. This leads to the formula

$$D = a^2/4\tau^* \qquad \text{......(19)},$$

where a is the distance between two neighbouring elementary spaces.

Langmuir also showed that if the time of transit between adjoining sites $(a/\bar{v})$ is not negligible compared with τ^*, then the formula must be modified to

$$D = a^2/4\,(\tau^* + a/\bar{v}) \qquad \text{......(20)},$$

where $\bar{v}$ is the average velocity parallel to the surface during migration. If τ^* is negligible compared with $a/\bar{v}$, then Langmuir gives

$$D = a\bar{v}/4 \qquad \text{......(21)},$$

which is similar to the formula for a two-dimensional gas when the free path is equal to a, but it is almost certain that for a dilute film the free path would be longer than a, and the formula (21) would have to be modified accordingly.

There remain now the important theoretical problems of calculating the times τ and τ^*. Lennard-Jones and Strachan(15) have obtained theoretical formulae for these quantities for the case when an adsorbed atom is activated from one vibrational state to another for motion perpendicular to the surface and the forces binding the atom to the surface are weak. Since there are forces coupling the adsorbed atom to the underlying solid, the problem is somewhat similar to that of the interaction of coupled oscillators, and energy may be expected to surge to and fro from one to the other. The problem is a little more complicated than that because a solid must be regarded as similar to an assembly of oscillators as in Debye's theory of specific heats. It appears that when an adsorbed atom has been excited to a higher vibrational level, and the temperature is low or (kT) small compared with the energy of excitation, it remains excited for a time of the order of one period of vibration; in a particular example this time was found to about 10^{-12} sec. The important result, however, is that for the range of temperature for which the formula is applicable, the time of excitation is nearly independent of the temperature. For high temperatures the theory indicates a shorter time of excitation inversely proportional to the temperature but the theory is hardly applicable under these conditions.

The formula for the time between successive excitations contains a Boltzmann (exponential) factor corresponding to the energy of activation.

Another mechanism of activation has been considered by Lennard-Jones and Goodwin(16). When the adsorbing solid is a metal, there will in general be an interaction between the free conduction electrons and the link between solid and adsorbed atom. A simple calculation by classical methods indicates that in a typical case a surface atom may suffer as many as 10^{15} collisions per sec. by the conduction electrons of a metal and since, according to modern views, these are moving with an energy of several volts, they provide an ample reservoir of energy from which adsorbed atoms may absorb energy. The general indication is that an atom will remain excited about 10^{-12} sec. before it falls to the next vibrational level and that this time is nearly independent of the temperature. The advantage of this mechanism is that larger quanta of energy can be communicated to the adsorbed link by a single process and atoms held by chemical bonds (such as hydrogen to a metal) can be thus activated. Several thermal quanta of energy would be required to be communicated to the link *simultaneously* to produce excitation. The corresponding formula for τ^* again contains a Boltzmann term appropriate to the energy of activation.

The author has calculated the dispersal of energy from an activated link also by classical methods, considering a linear array of similar atoms infinite in extent and supposing one of them displaced from its equilibrium position and then allowed to oscillate. It is found that after one complete period the potential energy of each of the links, which was disturbed initially, has fallen to a quarter of its initial value. The dispersal of energy along the chain is thus extremely rapid.

Apart from these mechanisms of deactivation a mobile atom may lose energy also by collision with another mobile atom or by collision with an adsorbed atom in a vibrating state. If the energy of activation for migration is small compared with kT, then most of the atoms will be in the migrating phase and collisions will be numerous. If, however, the energy of activation is large compared with kT, collisions between migrating atoms will be rare, and, if the concentration is not too large so that migration is not prevented by other adsorbed atoms, we may conclude that theory indicates at present that the duration of activation will be nearly independent of temperature.

A relation between the average values of τ and τ^* may be obtained by statistical methods. Let E_s denote an energy level of an adsorbed atom in a vibrating state and E_σ a level in the migrating state (each assumed for the moment to be discrete), and let $b_{s\sigma}$ be the probability per unit time of an activation from E_s to E_σ by the underlying solid. The function $b_{s\sigma}$ includes not only the matrix element of the coupling energy but also the probability that the solid is in a state suitable for the emission of the appropriate amount of energy. Let $b_{\sigma s}$ be the probability of the reverse process. Then in general for statistical equilibrium we must have

$$b_{\sigma s}=b_{s\sigma}\,e^{(E_\sigma-E_s)/kT} \qquad \text{......(22).}$$

The average value of τ^* is given by

$$\tau^*=\frac{\sum\limits_{s}\exp\left(-E_s/kT\right)}{\sum\limits_{s}\sum\limits_{\sigma} b_{s\sigma}\exp\left(-E_s/kT\right)} \qquad \text{......(23),}$$

where the summation in the denominator is over all pairs of states such that one is in the vibrating phase and one in the migrating phase. Similarly

$$\tau=\frac{\sum\limits_{\sigma}\exp\left(-E_\sigma/kT\right)}{\sum\limits_{s}\sum\limits_{\sigma} b_{\sigma s}\exp\left(-E_\sigma/kT\right)} \qquad \text{......(24).}$$

Using equation (22), we find that the two denominators are equal and so

$$\frac{\tau^*}{\tau}=\frac{\sum\limits_{s}\exp\left(-E_s/kT\right)}{\sum\limits_{\sigma}\exp\left(-E_\sigma/kT\right)}=\frac{f^*}{f} \qquad \text{......(25),}$$

where f and f^* are the partition functions relating to the migrating and vibrating phases respectively. This result is quite general whether the levels are quantized or not. Hence the formula for the diffusion coefficient D given in (18*a*) can be written

$$D=\alpha\bar{v}^2\tau f/(f+f^*) \qquad \text{......(26).}$$

In this formula $\bar{v}$ and τ are by definition *average* values, averaged over all migrating states; in fact, v is averaged twice, once over each migrating state and then over all such states. If the average lateral velocity in a state σ of energy E_σ during migration is $\bar{v}_\sigma$, and τ_σ the duration of time spent in this state in each elementary process, the general formula for D is

$$D = \frac{\alpha \sum_\sigma \bar{v}_\sigma{}^2 \tau_\sigma \exp(-E_\sigma/kT)}{(f+f^*)} \qquad \text{......(27).}$$

where the numerator is a sum over all migrating states. Equations (26) and (27) are equivalent, when $\bar{v}^2\tau$ in (26) is an average value, as just explained.

As an example of the application of the formula (26) we may consider the case when the periodic nature of the surface field is represented by a series of circular potential holes arranged regularly like a lattice. Let the height of the barrier separating these holes be V_0 and let the holes occupy a fraction r of the total surface area A. Then

$$f = A\,(2\pi mkT/h^2)\, e^{-V_0/kT} \qquad \text{......(28),}$$

and

$$f^* = rA\,(2\pi mkT/h^2)\,(1 - e^{-V_0/kT}) \qquad \text{......(29),}$$

so that for this model

$$D = \alpha \bar{v}^2 \tau / \{(1-r) + r \exp(V_0/kT)\} \qquad \text{......(30).}$$

When V_0 is large compared with kT, this may be written

$$D = (\alpha \bar{v}^2 \tau / r)\, e^{-V_0/kT} \qquad \text{......(31}a\text{),}$$

and when V_0 is small compared with kT, we have

$$D = \alpha \bar{v}^2 \tau \Big/ \left\{1 + r\frac{V_0}{kT}\right\} \qquad \text{......(31}b\text{).}$$

In the limiting case when V_0 becomes zero, the formula for D is

$$D = \alpha \bar{v}^2 \tau = \alpha \bar{v} l \qquad \text{......(31}c\text{),}$$

where τ is now the time between successive collisions in a two-dimensional gas and l is the mean free path. This is the usual form for the diffusion coefficient for a two-dimensional gas, and simple theories give for α the value of $\frac{1}{2}$.

As an example of the application of formula (31a), we may examine the experimental results obtained by Bosworth(13) for the migration of sodium atoms along a tungsten surface. Bosworth shows that his observations can be represented by the formula

$$D = aT^{\frac{1}{2}} e^{-b/T}$$

and from his figures it may be deduced that $b = 2750°$, which is equivalent to an energy of activation V_0 of 5500 cal./gram-atom or 0·24 eV. He does not give the value of a but it appears to be (5·64) 10^{-3}, and comparison with the theoretical formula gives

$$\alpha \bar{v}^2 \tau / r = (5{\cdot}64)\ 10^{-3}\ T^{\frac{1}{2}}.$$

Taking τ to be 10^{-13} sec. and α/r to be unity, we then get $\bar{v} = (2{\cdot}4)\ T^{\frac{1}{4}}\ 10^5$ cm./sec. and the free path ($l = \bar{v}\tau$) at room temperature is 10^{-7} cm. or about three or four times the length of a unit cell. A rough calculation gives the frequency of vibration of sodium about its position of equilibrium on the surface to be about 2.10^{-13} sec., so that τ may be longer than 10^{-13} sec. Taking it to be 10^{-12} sec., which is likely to be an extreme value, the free path comes out at about $3\cdot 10^{-7}$ cm., the equivalent of about nine unit cells. In any event the results of Bosworth, interpreted in terms of (31*a*) indicate that the free path is only slightly dependent on temperature. The factor which governs the rate of migration is the rate of activation to the migrating state.

Finally it may be mentioned that migration may occur when atoms collide with the surface from the vapour phase. It has been shown(18) that under certain conditions atoms may be diffracted at a surface without loss of energy in such a way that the atom afterwards runs along the surface. It is caught in one of the vibratory levels perpendicular to the surface, but the energy lost in the normal direction is taken up by the lateral motion and it speeds along in a migratory level. This mechanism satisfactorily explains the observations of Frisch and Stern(19) on the anomalous diffraction of helium by certain crystals and the calculations lead to the conclusion that the mean path of these atoms along the surface before being again diffracted into the vapour phase would be as long as 10^{-5} cm. As they are not so diffracted but are lost from the beam (thus producing the observed anomalies), the inference is that these migrating atoms lose energy either as a result of an encounter with an imperfection in the crystal or with an adsorbed atom or by their interaction with the solid and do not travel so far as 10^{-5} cm. This calculation therefore gives us an upper limit to a free path during migration and, as helium is a light atom and likely to migrate further than heavier atoms under similar conditions, we may infer that free paths are much shorter than 10^{-5} cm.

Migration at very low temperatures will not normally occur except at rates which are so slow as to be unobservable, but helium on certain solids appears to be an exception(20). Owing to the low energy barrier between neighbouring equilibrium positions and the small mass of the helium atom, penetration of the barrier may occur and calculations by quantum methods show that helium atoms may migrate almost like a two-dimensional gas however low the temperature.

REFERENCES

(1) Appleyard and Lovell. *Proc. phys. Soc.* above (1937).
(2) Lennard-Jones. *Trans. Faraday Soc.* **28**, 333 (1932).
(3) Cockcroft. *Proc. roy. Soc.* A, **119**, 293 (1928).
(4) Frenkel. *Z. Phys.* **26**, 117 (1924).
(5) Fowler. *Proc. Camb. phil. Soc.* **32**, 144 (1936).
(6) Bragg and Williams. *Proc. roy. Soc.* A, **145**, 699 (1934); **151**, 540 (1935).
(7) Bethe. *Proc. roy. Soc.* A, **150**, 552 (1935).
(8) Peierls. *Proc. Camb. phil. Soc.* **32**, 471 (1936).
(9) Lennard-Jones and Devonshire. (To be published shortly.)
(10) Volmer. *Trans. Faraday Soc.* **28**, 359 (1932).

(11) (*a*) LANGMUIR and TAYLOR. *Phys. Rev.* **40**, 463 (1932).
(*b*) TAYLOR and LANGMUIR. *Phys. Rev.* **44**, 423 (1933).
(12) BRITTAIN and BECKER. *Phys. Rev.* **43**, 428 (1933).
(13) BOSWORTH. *Proc. roy. Soc.* A, **150**, 58 (1935), **154**, 112 (1936).
(14) (*a*) GEHRTS. *Z. tech. Phys.* **15**, 456 (1934).
(*b*) BRESLER, TALMUD and TALMUD. *Phys. Z. Sowjet,* **4**, 864 (1934).
(*c*) SCHWARZ. *Z. phys. Chem.* **168**, 241 (1934).
(*d*) ALTY and CLARK. *Trans. Faraday Soc.* **31**, 648 (1935).
(15) LENNARD-JONES and STRACHAN. *Proc. roy. Soc.* A, **150**, 442 (1935).
(16) LENNARD-JONES and GOODWIN. (To be published shortly.)
(17) LENNARD-JONES and DEVONSHIRE. *Proc. roy. Soc.* A, **156**, 14, equation (29), (1936).
(18) LENNARD-JONES and DEVONSHIRE. *Proc. roy. Soc.* A, **158**, 253 (1937).
(19) FRISCH and STERN. *Z. Phys.* **84**, 430 (1933).
(20) LENNARD-JONES and DEVONSHIRE. *Proc. roy. Soc.* A, **158**, 242 (1937).

DISCUSSION OF THE PAPERS BY FINCH, APPLEYARD AND LENNARD-JONES

Reported by E. T. S. APPLEYARD

ONE of the important questions discussed was the cause of the negative temperature coefficient of resistance observed in so many thin films but not in the case of the alkali metals.

Dr Lovell gave an account of some preliminary results which he had obtained with thin films of thallium deposited under the same high vacuum conditions already used by him for the alkali metals. In the region of thickness between 20 and 30 A., the resistivity of the films was about 10^4 times that of the bulk metal, and they showed a negative temperature coefficient. But both their resistivity and their temperature coefficients were much below those obtained previously by Cosslett using the similar metal indium in a vacuum of about 10^{-5} mm. of mercury. On this account Dr Lovell believed that the idea of Cosslett that the negative temperature coefficient was in some way due to gas adsorbed or occluded in the film was strongly supported, more especially since he himself had been able to alter both the resistivity and the temperature coëfficient of his thallium films by altering their rate of deposition.

Dr de Boer was unable to accept the general explanation of negative temperature coefficients given above. On the experimental side he pointed out that the results he had obtained with molybdenum were quite reproducible in successive experiments. Moreover, certain unpublished results obtained recently in his laboratory with evaporated tungsten films exactly reproduced the results obtained many years ago by Reinders and Hamburger. It seemed to him almost inconceivable that this agreement could be obtained if the residual gas played any important part. Moreover, he had found that the influence of gas upon the resistivity of the films once formed was unimportant except in the case of oxygen, and that even here the influence was not appreciable provided that the films were kept at liquid air temperatures. He adhered to the view that the thin films of molybdenum and tungsten showed a different atomic spacing from those of the bulk metal, at any rate in the early layers, and that as a consequence of this larger spacing (for which, as yet, there was admittedly no other experimental evidence) the thin films behaved like a semi-conductor. The lower conductivity could arise either as a result of the raising of the potential barriers between successive metallic ions, or from a diminished overlapping of the electronic bands; both would be favoured by an increased interatomic spacing. He suggested that a direct experimental measurement of the distribution of the electrons in the bands (as compared with the distribution in the bulk metal) might be obtained if Skinner's* method of investigating the X-ray emission spectrum were applied to very thin metallic films.

Dr Fuchs remarked that for monovalent metals a very considerable increase in atomic spacing would be necessary to produce the transition from the metallic to the semi-conducting state, for the potential barrier between successive lattice points was not at all sensitive to small increases of spacing.

Dr Klatzow said that some experiments of his own on the electrical resistance of composite caesium films such as are employed in commercial photoelectric practice had led him to believe that (in agreement with the view of Lovell and Appleyard) their high resistivity and negative temperature coefficients were both to be explained in terms of a disintegrated structure. He suggested that in this case the current was carried across the gaps in the film by cold emission of electrons, i.e. by the movement of electrons across the gaps under the action of the applied electric field (cf. Frenkel, *Phys. Rev.* **36**, 1613 (1930), Ehrenberg and Hönl, *Z. Phys.* **68**, 289 (1931)). On such a theory an increase in the work function would decrease the current. This notion was made more reasonable because on evaporating a thin layer of silver over the composite layer its resistance actually increased. Silver deposition in this way was known quite independently to raise the work function and to diminish the cold-emission of such composite surfaces.

The above discussion clarified the points of difference between the possible hypotheses used to explain the negative temperature coefficient, but no definite conclusions could be drawn as to which one was correct.

Another point discussed was the role of agglomeration in thin films.

Prof. Fowler criticized Dr Appleyard's criterion for agglomeration. He remarked that although it led to the right results when applied at these low temperatures, the general condition for any isothermal process to be possible was of course that the free energy (and not the potential energy) should diminish.

Dr Cockcroft remarked that the values given in table 2 of Dr Appleyard's review should be accepted with reserve since they were obtained in the days before vacuum technique had approached its present level and the surfaces must have been very dirty judged by present standards. This was proved by the fact that the latent heat of evaporation was the same for surfaces of copper, silver and glass. He asked whether the mercury films described in the report were affected by previous heat treatment of the substrate. Dr Appleyard replied that prolonged heat treatment of the type given by Lovell seemed to make no difference whatsoever to the critical thickness or the shape of the resistivity curve, and that this was consistent with the view that mercury-on-pyrex was an extreme case of type-III films.

Dr Skinner observed that zinc, cadmium and mercury seemed to stick with great difficulty to celluloid surfaces. In these cases he had been successful in obtaining films only by saturating the substrate with dirt from the backing vacuum.

Dr de Boer drew attention to the results of some experiments carried out in his laboratory on the electrical resistance of evaporated layers of alkali halides coated with adsorbed films of caesium. The halides have a lamellar and labyrinthine structure; the adsorbed layers of caesium on the surfaces of the lamellae are superposed upon each other and so absorb enough light to be visible. It was found that the electrical resistance of such a composite layer changed only very slowly as the adsorption of caesium continued which suggested that agglomeration might be taking place on top of a stable monolayer. Dr Appleyard said that this effect was perhaps somewhat similar to that observed with caesium-on-pyrex. In this case the early layers appeared to be more stable than thicker layers, which suggested that agglomeration here also took place most rapidly with the second, third . . . etc. layers, the first layer agglomerating only slowly.

---

* O'Bryan and Skinner, *Phys. Rev.* **45**, 370 (1934). Skinner and Johnson, *Proc. roy. Soc.* A (in Press).

The discussion on agglomeration continued after the paper of Prof. Lennard-Jones. In reply to questions Prof. Lennard-Jones said that he was quite unable to understand how mercury-on-pyrex could possibly show the high mobility at low temperatures suggested by the experimental results. There was no analogy (as Dr Appleyard had implied) between this case and that of helium-on-lithium fluoride previously discussed by him, for the finite mobility at all temperatures above absolute zero obtained with helium depended entirely upon the small mass of the helium atom. It was, of course, possible in principle to calculate the interaction of a mercury atom with a silica surface, and in this way to obtain values for the latent heat and the activation energy, but he would be surprised if the values obtained were low enough to account for the experimental results. A brief discussion then took place on the proper assumptions to be used in calculating the forces in this case.

The general conclusion seemed to be that the role of agglomeration was extremely important in accounting for the high resistance of metal films, and that the criteria for agglomeration put forward by Prof. Lennard-Jones and Dr Appleyard provided a starting point for understanding the process. In spite of this, the paucity of data on the latent heats of evaporation of metals from insulating surfaces prevented anything but the most general qualitative conclusions being drawn in particular cases.

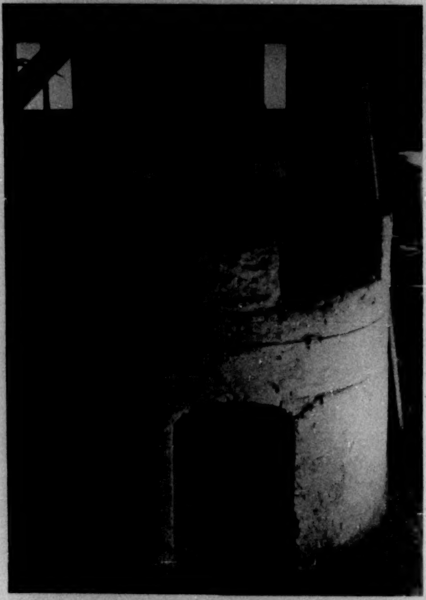
The sputtered films obtained by Dr Féry were also discussed with interest. Prof. Finch mentioned that certain experiments he had performed some time ago were in agreement with the extended investigations of Dr Féry. He too had been able to obtain a catalytic deposit by suitable sputtering methods, and he had found like Dr Féry that the presence of H_2 or H_2 and O_2 in the discharge inhibited the formation of catalytic platinum. He drew attention also to the experimental fact that metal foils heated in air showed a great tendency to form a single crystal, but metallic deposits on an insulating substrate did not.

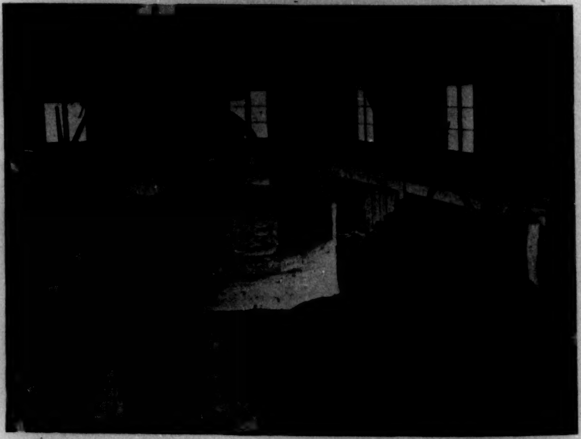
On Dr Féry's paper Dr Appleyard remarked that it was extremely valuable in enabling us to understand how the black-white transition in platinum could account for the extravagantly different results of previous workers on sputtered films. He remarked that although the temperature coefficient as ordinarily defined diminished greatly on annealing, nevertheless the resistivity change per degree shown in Dr

Féry's work remained fairly constant and approximately the same as for the bulk metal. This could perhaps be accounted for by assuming a diminishing "restwiderstand".

Dr de Boer then showed another case of an unstable film, in this instance silver evaporated on a liquid air cooled surface. This film on heating suffered an almost explosive disintegration accompanied by a flash of light.

CAMBRIDGE: PRINTED BY WALTER LEWIS, M.A., AT THE UNIVERSITY PRESS





Frontispiece